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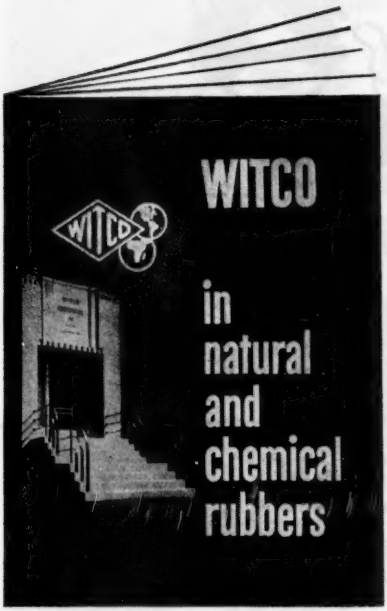

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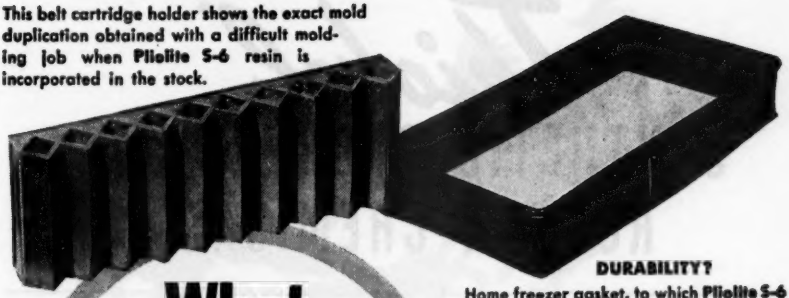

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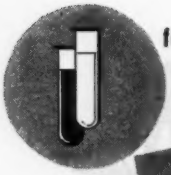

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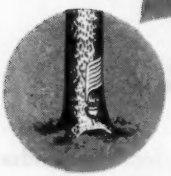

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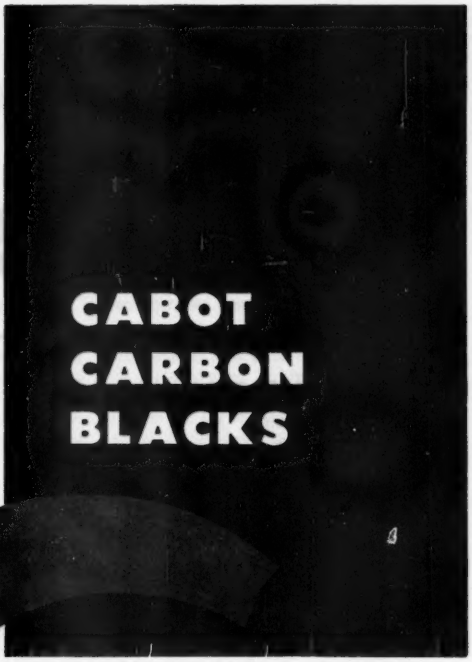

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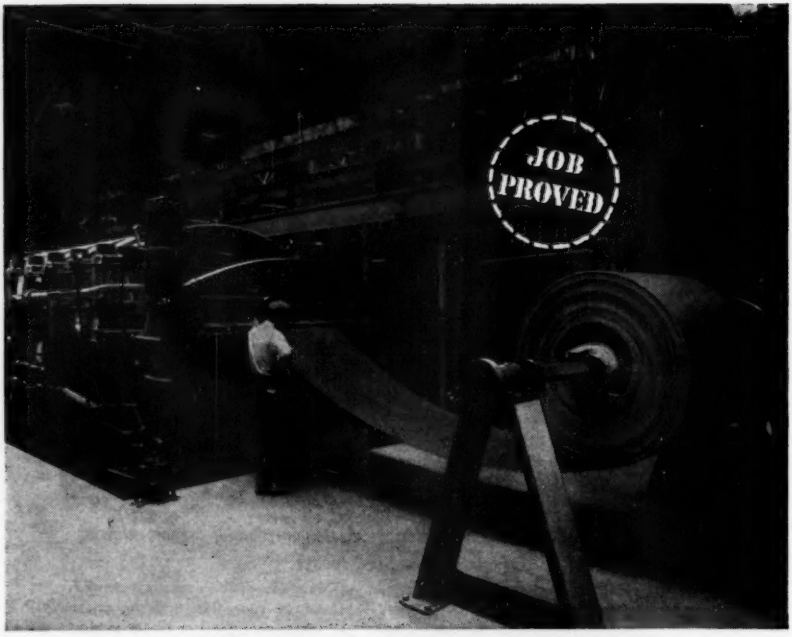

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Chairman....T. J. Gorman, Quaker Rubber Corp., Philadelphia, Penna. *Vice-Chairman*....H. J. Reid, L. H. Gilmer Co., Division of U. S. Rubber Co.,

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SOUTHERN OHIO

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Papers Review—C. C. Davis, J. H. Fielding, C. R. Haynes.

Program—G. H. Swart (Chairman), A. M. Clifford, A. E. Juve, G. E. P. Smith, Jr., A. W. White.

Teller—R. W. Kixmiller (Chairman), E. B. Curtis, A. R. Davis.

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY DETROIT, MICHIGAN, APRIL 19–21, 1950

The 56th Meeting of the Division of Rubber Chemistry was held, under the chairmanship of F. W. Stavely, in Detroit, Michigan, in conjunction with the 117th Meeting of the American Chemical Society. The Division headquarters was at the Book-Cadillac Hotel, at which both technical sessions and banquet were held.

Local arrangements were in the hands of a committee headed by G. M. Wolf, General Chairman, assisted by G. F. Lindner, F. H. Jankowski, E. S. Knorr, G. R. Cuthbertson, W. J. Simpson, J. C. Dudley, C. J. Edwards, Jr., T. W. Halloran, H. W. Neale, E. V. Hindle, E. W. Hafferd, G. P. Hollingsworth, J. T. O'Reilly, W. F. Bauer, R. J. Shroyer, and E. J. Kvet.

About 650 members and guests registered for the meeting, but many in addition registered earlier with other Divisions. The banquet attendance was about 725.

The 25-Year Club, comprising those who have been associated professionally with the rubber industry for 26 years or longer, met at an informal luncheon, which was in charge of E. J. Kvet. Six new members joined the ranks of the Club.

The Directors held two meetings, and accepted the invitation of the newly sponsored Washington Group to hold the Spring Meeting of 1951 on February

28, and March 1–2 in Washington, D. C. The Fall Meeting of 1951 will be held as a part of the Jubilee Meeting of the American Chemical Society in New York.

L. V. Cooper, Chairman of the Membership Committee, reported 1774 Members and 270 Associates, a total of 2044, in addition to numerous company and contributing members.

At the business meeting, Chairman Stavely announced the loss by death of two members of the Division: Robert R. Miller of Detroit, Michigan and G. W. Sneed of St. Louis, Missouri.

The slate for officers and directors for the following year, presented by W. W. Vogt for the Nominating Committee, under the Chairmanship of S. M. Cadwell, was approved without modification.

The Chairman reported that another volume of the "Bibliography" would be forthcoming the latter part of this year.

The Bylaws of the Division, revised under the supervision of S. G. Byam, were presented to the Division and were accepted unanimously.

The following papers were presented.

(1) Reclaiming Agents for Natural and Synthetic Rubber. I. Solvent Naphtha. D. S. Le Beau (Midwest Rubber Reclaiming Co.).

(2) Some Problems Involved in the Grading and Testing of Natural Rubber. II. Mastication and Compounding. R. F. Blackwell, C. M. Blow, W. P. Fletcher, L. Mullins, and R. I. Wood (British Rubber Producers' Research Association).

(3) Effect of Air on Banbury Breakdown of Low Temperature Polymers. G. J. Tiger, M. H. Reich, and W. K. Taft (University of Akron).

(4) Factors Influencing the Dispersion of Styrene-Butadiene Resins. H. S. Sell and R. J. McCutcheon (Goodyear Tire & Rubber Co.).

(5) An Autopneumatic Apparatus for Measuring Stress Relaxation. C. S. Wilkinson, Jr., and S. D. Gehman (Goodyear Tire & Rubber Co.).

(6) Effect of Ammonia on the Electroplating of Neoprene Latices. D. T. Williams and S. Palinchak (Battelle Memorial Institute).

(7) Esters of Dialkyldithiocarbamic Acids as Plasticizers for Acrylonitrile Rubbers. A. W. Campbell (Commercial Solvents Corp.).

(8) Tetramethylthiuram Disulfide Vulcanization of Extracted Rubber. I. Essential Features of Tetramethylthiuram Vulcanization. A. E. Juve, D. Craig, and W. L. Davidson (B. F. Goodrich Co.).

(9) Tetramethylthiuram Disulfide Vulcanization. II. Radioactivity Studies Bearing on the Tetramethylthiuram Disulfide Vulcanization Mechanism. W. L. Davidson, D. Craig, A. E. Juve, and I. G. Geib (B. F. Goodrich Co.).

(10) Tetramethylthiuram Disulfide Vulcanization. III. The Nature of Zinc Activation. D. Craig, A. E. Juve, and W. L. Davidson (B. F. Goodrich Co.).

(11) A New Class of Organic Accelerator-Activators Derived from Amic Acids. M. C. Throdahl, R. O. Zerbe, and D. J. Beaver (Monsanto Chemical Co.).

(12) Oxidation of Olefins Representing Some Structural Units of GR-S. W. C. Warner and J. R. Shelton (Case Institute of Technology).

(13) Alfin-Catalyzed GR-S Type Polymers. H. Goldsmith and W. K. Taft (University of Akron).

(14) Recent Developments in GR-S Latex Polymerized at Low Temperatures. H. S. Smith, H. G. Warner, C. B. Westerhoff, and L. H. Howland (U. S. Rubber Co.).

(15) The Structure of Neoprene Type W. W. E. Mochel and J. B. Nichols (E. I. duPont de Nemours & Co.).

(16) Aging Studies Redox Polymers. C. R. Parks, J. O. Cole, and J. D. D'Ianni (Goodyear Tire & Rubber Co.).

(17) Polymerization Recipes for 41° F Sugar-Free Redox Systems. V. C. Neklutin, C. B. Westerhoff, and L. H. Howland (U. S. Rubber Co.).

(18) Study of the Aqueous Dispersion Characteristics of Carbon Blacks. E. M. Dannenberg and K. P. Seltzer (Godfrey L. Cabot, Inc.).

(19) New Developments in Masterbatching Carbon Black with GR-S Latices. J. W. Adams, W. E. Messer, and L. H. Howland (U. S. Rubber Co.).

(20) Carbon Gel As Revealed by the Electron Microscope. W. A. Ladd and M. W. Ladd (Columbian Carbon Co.).

(21) The Mechanism of Reënforcement. Nature of the Interaction Between Carbon Black and Polymer in Cured Elastomers. R. S. Stearns and B. L. Johnson (Firestone Tire & Rubber Co.).

(22) Electrical Resistivity of Various Carbon Blacks in Natural, GR-S, Cold, and Butyl Rubbers. L. R. Sperberg, G. E. Popp, and C. C. Baird (Phillips Chemical Co.).

(23) Effect of Carbon Blacks on Heat Transfer Characteristics of Vulcanizates. L. R. Sperberg, L. H. Harrison, and J. F. Svetlik. (Phillips Chemical Co.).

(24) Effect of Colloidal Noncarbon Pigments on Elastomer Properties. E. Schmidt (Firestone Tire & Rubber Co.).

C. R. Haynes, *Secretary*

NEW BOOKS AND OTHER PUBLICATIONS

The Physics of Rubber Elasticity. L. R. G. Treloar. Oxford University Press, 114 Fifth Ave., New York 11, N. Y. Cloth, 5½ by 8½ inches, 262 pages. Price, $6.—This is the fourth volume in a series, "Monographs on the Physics and Chemistry of Materials," intended to summarize recent results of academic research in materials and related subjects. This book is a commendable attempt to set down in concise form a review of recent developments in rubber elasticity from both the theoretical and experimental aspects. The statistical or kinetic theory of elasticity is developed and shown satisfactorily to account for the fundamental mechanical and photoelastic properties of rubber. The fundamental concepts of the subject are presented in a systematic form, without undue emphasis on mathematical treatment, and with many diagrams and tables as illustrations.

Individual chapters are devoted to the following subjects: general physical properties of rubbers; internal energy and entropy changes on deformation; elasticity of long-chain molecules; elasticity of a molecular network; experiments on simple types of strain; refinements to the theory in the region of very large strains; deviations from the statistical theory; photoelastic properties of rubber; crystallization in stretched and unstretched rubber; crystallization and mechanical properties; stress relaxation and flow; dynamic properties of rubbers; and solution of problems involving large elastic strains. Each chapter begins with an introduction, presents applicable theoretical and experimental work, and concludes with a section summarizing these developments and current status

of the subject. The book concludes with a bibliography and author and subject indices. [From the *India Rubber World.*]

ELASTOMERS AND PLASTOMERS, THEIR CHEMISTRY, PHYSICS, AND TECHNOLOGY. Volume II. Manufacture, Properties, and Applications. Edited by R. Houwink. Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y. Cloth, 6¾ by 10 inches, 530 pages. Price, $7.—This volume, the second in a series of three, is a symposium of methods used in the manufacture of plastics and, as such, will be of special value to students in the high-polymer field and for use as a reference. There are 13 chapters with 19 contributors, of whom 13 are from Western European nations. Consequently much of the material presented is based on European experience, but is quite sound within these limits. The discussion of manufacturing procedures is mainly qualitative, but comprehensive and well presented. Each chapter includes a summary and bibliography, and added value is derived by the use of many illustrations, tables, and graphs.

Topics covered include phenol-formaldehyde plastomers, synthetic resin ion exchangers, urea and melamine resins, polymers from ethylene derivatives, cellulose derivatives, protein plastics, fibers from proteins, synthetic polyamides, silicone polymers, alkyd resins, natural resins and their derivatives, derivatives of natural rubber, synthetic rubbers, and asphalts. The chapters on natural rubber derivatives and synthetic rubbers are by T. R. Dawson, respectively. A comprehensive subject index is included in the volume. [From the *India Rubber World.*]

A CHEMISTRY OF PLASTICS AND HIGH POLYMERS. Patrick D. Ritchie. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. Colth, 5½ by 8½ inches, 296 pages. Price, $4.50.—This book is a departure from the usual text on high polymers in that it emphasizes the organic chemistry of polymeric materials rather than the theoretical approach to the subject. As such, it fulfills a definite need of a one-volume book giving a comprehensive treatment of polymer chemistry from the synthetic and structural aspects. The physical chemistry is discussed in a qualitative and nonmathematical manner, and other fundamentals are given brief but adequate treatment. Although requiring a knowledge of chemistry at about the graduate level, this book gives a highly satisfactory survey of polymer chemistry and shows the breadth of the field, summarizes raw material sources and synthetic methods, and surveys recent advances.

The presentation is well written, systematic in outline, and illustrated with many structural diagrams. The 16 chapters cover the following subjects: plastics and high polymers; polyfunctional molecules and polymerization; mechanism and kinetics of polymerization; synthetic addition high polymers; polyesters, polyamides, and polyethers; phenoplastics; aminoplastics; natural high polymers, including proteins, cellulosics, lignins, and rubbers; drying oils; mineral and inorganic high polymers; relation between structure and polymer properties; and high polymers and plastics. A list of references for further reading is appended to each chapter, and the book concludes with an index of trade names and author and subject indices. [From the *India Rubber World.*]

STRETCHING HIGHWAY DOLLARS WITH RUBBER ROADS. By Harry K. Fisher. Natural Rubber Bureau, 1631 K Street, N.W., Washington 6, D. C.

6×9 in. 28 pp.—A brief progress report on recent developments in the use of natural rubber for road construction is presented. The booklet discusses the first test strips laid down in Virginia, Ohio, Texas, Minnesota, and Canada. The techniques used on each of the test strips, the recipes, and results to date are elaborated upon. Charts, tables, photographs, and drawings illustrate the text material. [From the *Rubber Age* of New York.]

ASTM Standards on Adhesives. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6×9 in. 60 pp. $1.25.—Sponsored by ASTM Committee D-14 on Adhesives, this booklet contains in convenient form all 15 ASTM standards relating to this field. Test methods cover resistance of adhesive bonds to chemical reagents; tensile properties of adhesives; applied weight per unit area of dried adhesive solids and liquid adhesive; peel or stripping strength of adhesives; strength properties of adhesives in shear by compression loading and in plywood type construction in shear by tension loading; viscosity and total solids content of rubber cement; sampling and testing latices of natural and synthetic rubbers; testing rubber adhesives. There is a recommended practice for determining the effect of artificial (carbon-arc type) and natural light on the permanence of adhesives. Also included are definitions of terms relating to adhesives. New material in this edition includes tests for impact strength of adhesives; strength properties of metal-to-metal adhesives in shear by tension loading; and cleavage strength of metal-to-metal adhesives. [From the *Rubber Age* of New York.]

American Cotton Handbook. Second Edition. G. R. Merrill, A. F. Macormac, and H. R. Mauersberger. Textile Book Publishers, Inc., 303 Fifth Ave., New York 16, N. Y. Cloth, 5 by 7½ inches, 962 pages. Prices, $9.50 in United States and Canada; $10.50 all other countries.—This second edition of the handbook provides an up-to-date practical text and reference book on the entire cotton textile industry. To retain the convenient handbook size, some of the subjects covered in the previous edition have been eliminated, including the appendix on statistical methods, the glossary, and the chapters on cotton gray goods constructions, sewing threads, weaves, goods designing, and laundering of cotton materials. In place of these subjects there are now new, and expanded chapters dealing with recent developments in the field.

Chapters are devoted to historical background; economic and statistical background of cotton growing and manufacturing; cellulose and the cotton fiber; cultivation and varieties of cotton plants; ginning, classing, and marketing; opening and picking; carding and combing; drawing and roving; standard and long draft spinning; winding and twisting; spooling, warping, and slashing; weaving of cotton gray goods; knit goods manufacture; bleaching and other predyeing processes; cotton dyeing; printing piece goods; finishing cotton goods; physical and chemical testing; and nomenclature of cotton dyes. A bibliography of books and other publications; and listing of trade associations, films, and magazines; and a comprehensive subject index complete the book. [From the *India Rubber World.*]

Russian–English Technical and Chemical Dictionary. By Ludmilla Ignatiev Callaham. John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. (London: Chapman & Hull, Ltd.), 1947. xvii+794 pp. 19.5×14 cm. Price, $10.00.—After her graduation from Barnard College with a degree

in chemistry Mrs. Callaham began to translate technical Russian articles and to abstract them for American journals. For her own convenience she compiled a vocabulary of technical terms which soon outgrew chemistry and began to include words from all the related scientific and engineering fields. This dictionary is the result of a systematic expansion of that vocabulary.

The volume consists of a short introduction to the Russian alphabet and to the structure of Russian words and sentences, together with a list of common Russian technical word endings, and then proceeds directly to the 794 pages of word listings. The dictionary naturally assumes a fair reading knowledge of Russian, and therefore does not undertake to teach the Russian language, but only to list the various types of words expected to appear in technical articles devoted to aeronautics, radio technology, meteorology, agriculture, medicine, physics, chemistry, and mathematics. The various branches of chemistry are given the most complete coverage, but the volume lives up to its general title.

The type, format and paper are good, and the dictionary undoubtedly would be a valuable addition to the library of the present-day chemist. It is perhaps unfortunate that the cost of setting up so complete a dictionary in Russian type, plus the large amount of labor required in the compilation and proof-reading, requires so high a retail price; most chemists will find it somewhat steep for personal acquisition, but may be in a position to recommend purchase of the dictionary for use in chemical libraries. The reviewer recommends it highly for this purpose. [Eugene G. Rochow in the *Journal of the American Chemical Society.*]

MASTICATION AND COMPOUNDING OF NATURAL RUBBER IN AN OXYGEN-FREE ATMOSPHERE *

C. M. Blow and R. I. Wood

British Rubber Producers' Research Association, Welwyn Garden City, England

MASTICATION AND THE EFFECT OF PLASTICIZERS

INTRODUCTION

The important role played by oxygen in the breakdown of rubber during mastication has been established by Cotton and Busse[1]. However, the effect of plasticizers, and in particular chemical plasticizers, often incorrectly termed "peptizers", in the absence of oxygen has received only slight attention[2].

This subject and the closely related question of the production of vulcanizable compounds in an inert atmosphere appeared to need a fuller investigation; and in this paper are recorded some results and observations obtained from experiments conducted in an atmosphere of nitrogen.

The first part of the paper deals with the relative effect of the mastication of natural rubber in air and in nitrogen over a temperature range from 50° to 140° C; together with a brief survey of the effect of common plasticizers and softeners, and a more detailed treatment of two chemical plasticizers, mercaptobenzothiazole and *o-o'*-dibenzamidodiphenyl disulfide.

The second part covers the production of a number of pure-gum compositions under nitrogen and comparison of the physical properties of the resulting vulcanizates with those of similar compounds obtained by normal air compounding.

EXPERIMENTAL

Apparatus.—The apparatus employed was a small laboratory-type (Size B) Bridge Banbury internal mixer, with a capacity of about 500 grams of raw rubber. The machine was suitably modified for operating under nitrogen by fitting a metal top plate with inlet and outlet nipples, and by sealing all other outlets, *e.g.*, chamber seams, etc., with asbestos putty. Efficient sealing of the floating bearings employed on this type of machine could not be achieved, and it was therefore decided to operate with a small excess pressure of nitrogen inside the chamber, equivalent to 1 inch of water. This excess pressure was recorded by means of a water manometer connected to the outlet nipple, and although some fluctuation occurred during operation caused by changes in bearing clearance, the pressure never dropped below ½ inch of water, and a fairly constant mean pressure could be maintained. Since complete displacement of air by nitrogen would be very unlikely under these conditions, no attempt was made to degas the rubber before mastication and oxygen-free grade cylinder nitrogen (less than 10 volumes of oxygen per million volumes) was used, without further purification. A plunger bar was attached to the top plate to prevent the charge from riding off the rotors during mastication, and as

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 25, No. 5, pages 309–327, February 1950.

it was necessary to introduce a full charge and clamp the machine down before setting it in motion, a batch weight of 200 grams of rubber was used throughout the mastication experiments to avoid stalling the motor when operating from the cold.

Determination of degree of breakdown.—Degree of breakdown was measured on a standard Mooney viscometer, operating at a temperature of 100° C, with a disc rotor (1½ inches diameter) revolving at a speed of 2 revolutions per minute. The samples were allowed to stand in air for 24 hours after mastication, before being tested. The values recorded are dial readings after 1 minute warming up and 3 minutes running.

Reproducibility of results.—A preliminary set of experiments was carried out to determine the reproducibility of results and the period of sweep out with nitrogen needed to ensure removal of air from the apparatus before commencing mastication (see Table 1). A 10-minute period of sweep out was established as satisfactory, and was used in all subsequent mastication experiments under nitrogen.

TABLE 1

REPRODUCIBILITY OF RESULTS

20 Minutes' Mastication

Atmosphere	Time of sweep out (min.)	Mooney viscometer readings		
Air		40.5	42.0	42.0
Nitrogen	5		103.5	
	10		102.5	
	15		102.5	

Mastication of smoked sheet.—Mastication was carried out in air and in nitrogen: (1) with cold water flowing through the casing and rotor, (2) with open steam through the casing and rotor, and (3) with steam at 40 lb. per sq. in. through the casing and rotor.

With cold mastication an approximate estimate of the temperature reached by the rubber during working was obtained by embedding a needle pyrometer in the center of the mass immediately on removal from the mixer. Temperature readings between 43° and 58° C were observed, nitrogen mastication giving in every case higher values than air mastication, the mean difference being 5° C.

The results of mastication in air and in nitrogen are shown in Figure 1. Experiments in the cold and at 100° C were carried out with a sample of smoked-sheet rubber with an initial Mooney viscosity of 97 to 98. The work at 142° C was with smoked sheet rubber having an initial Mooney viscosity of 92.

The results obtained in air are consistent with the well established practice of cold mastication for maximum breakdown and mastication at about 100° C for minimum breakdown.

The very slight breakdown under nitrogen at 100° and 142° C suggests that breakdown in air is entirely oxidative, but the initial increase in viscosity followed by breakdown as recorded at 50° C means that the possibility of some other parallel mechanism, such as mechanical breakdown, cannot be ruled out. A further investigation of the effect of mastication in the cold under nitrogen was, therefore, carried out over a longer period using a fresh sample of No. 1x ribbed smoked sheet rubber having a Mooney viscosity of 100; and also a batch of U.S.F. rubber[3] of Mooney viscosity 87.

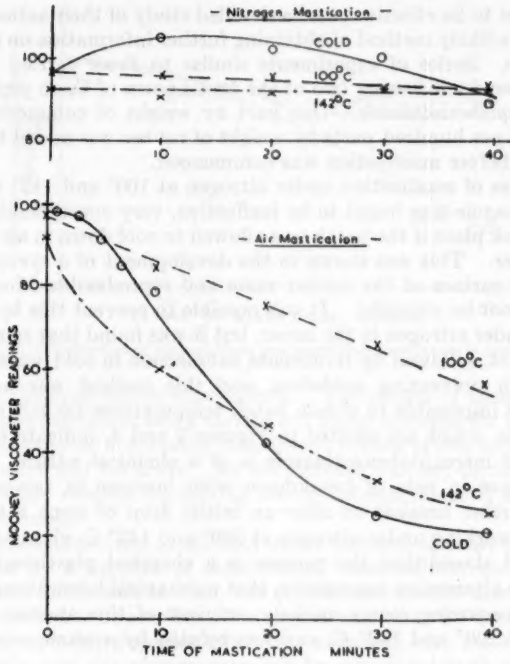

FIG. 1.—Mastication of smoked sheet.

The results on the three rubbers are shown in Figure 2. None gives any indication of immediate breakdown, but the well marked initial increase in viscosity shown by the first sample of smoked sheet and by the U.S.F. rubber appears to be absent in the case of the second smoked sheet sample.

Mastication of smoked sheet rubber in the presence of the socalled peptizers.—During the past decade many chemicals have appeared which have the property of accelerating the breakdown of raw rubber during mastication, particularly at temperatures of the order of 120° to 140° C. These are in many instances referred to as peptizers, a term which suggests a physical or mechanical action. Some evidence has already been advanced to suggest that these compounds

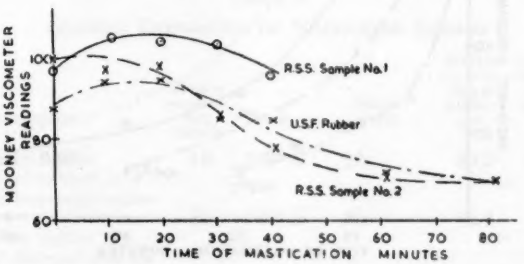

FIG. 2.—Cold mastication of raw rubber in nitrogen.

require oxygen to be effective[4], and a detailed study of their action under nitrogen appeared a likely method of obtaining further information on their plasticizing properties. Series of experiments similar to those carried out with raw rubber were conducted using two of the best known of these peptizers.

(1) *Mercaptobenzothiazole.*—One part by weight of commerical mercaptobenzothiazole per hundred parts by weight of rubber was added to the batch in the Banbury before mastication was commenced.

In the cases of mastication under nitrogen at 100° and 142° C, where mercaptobenzothiazole was found to be ineffective, very considerable oxidation of the rubber took place if the batch was allowed to cool down in air after removal from the mixer. This was shown in the development of a syrupy very sticky film over the surface of the rubber mass and reproducible Mooney viscosity figures could not be obtained. It was possible to prevent this by cooling down each batch under nitrogen in the mixer, but it was found that removal from the mixer while hot, followed by immediate submersion in cold water, proved just as effective in preventing oxidation, and this method was adopted. This effect made it impossible to obtain batch temperatures for hot mastication.

The results, which are plotted in Figures 3 and 4, indicate that in air the main effect of mercaptobenzothiazole is of a chemical nature, there being a marked increase in rate of breakdown with increase in temperature. The absence of further breakdown after an initial drop of some 8 to 10 Mooney points, when working under nitrogen at 100° and 142° C, gives confirmation of this view and shows that the process is a chemical plasticization requiring oxygen. The alternative explanation that mechanical lubrication of the rubber molecules is occurring seems unlikely, in view of this absence of continued breakdown at 100° and 142° C, and was refuted by acetone extraction of the

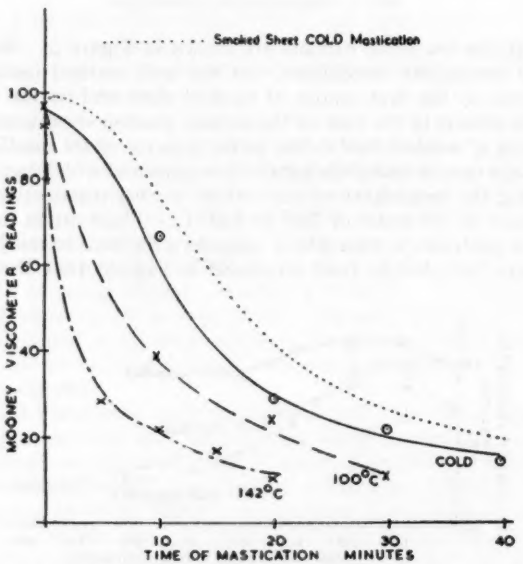

FIG. 3.—Mastication of smoked sheet and mercaptobenzothiazole in air.

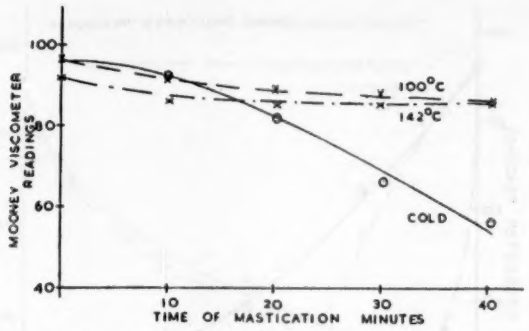

FIG. 4.—Mastication of smoked sheet and mercaptobenzothiazole in nitrogen.

rubbers from the mastication experiments. The results of these are shown in Table 2, acetone extraction being carried out under nitrogen for 24 hours. The increase in viscosity of a normally masticated rubber is due to the removal of the natural resins and fat acids. As the increase was not significantly greater in the case of the rubbers containing mercaptobenzothiazole, any lubrication effect must be small.

The breakdown recorded in the cold under nitrogen appears anomalous. It was confirmed by a number of independent observations, and did not take place if an inert filler, such as clay, was substituted for the mercaptobenzothiazole, *i.e.*, it could not be attributed to oxygen carried in by the added powder. As will be shown later, a similar effect was obtained with *o-o'*-dibenzamidodiphenyl disulfide, and this phenomenon will be considered further in the general discussion of the mastication data.

(2) *o-o'-Dibenzamidodiphenyl disulfide.*—The recent appearance on the commercial market of *o-o'*-dibenzamidodiphenyl disulfide allowed the comparison of its properties with those of mercaptobenzothiazole to be made. A series of experiments similar to the above was carried out, using 1 part by weight of *o-o'*-bidenzamidodiphenyl disulfide per 100 parts by weight of rubber. As with mercaptobenzothiazole, it was found necessary to cool down under water, after mastication under nitrogen at 100° and 142° C, to prevent surface oxidation. The results are plotted in Figures 5 and 6.

The general effect of *o-o'*-dibenzamidodiphenyl disulfide is similar to that of mercaptobenzothiazole. In air, below 100° C, it is a little less efficient, and

TABLE 2

ACETONE EXTRACTION OF MASTICATED RUBBER

Composition	Time of mastication (min.)	Temp.	Atmosphere	Mooney viscometer reading: Before extraction	Mooney viscometer reading: After extraction	Mooney viscometer reading: Increase
Smoked sheet rubber	10	100° C	Air	89.5	95.0	5.5
Smoked sheet rubber + 1 part of mercaptobenzothiazole	10	100° C	Air	38.0	45.0	7.0
Smoked sheet rubber + 1 part of mercaptobenzothiazole	40	Cold	Nitrogen	56.0	63.0	7.0

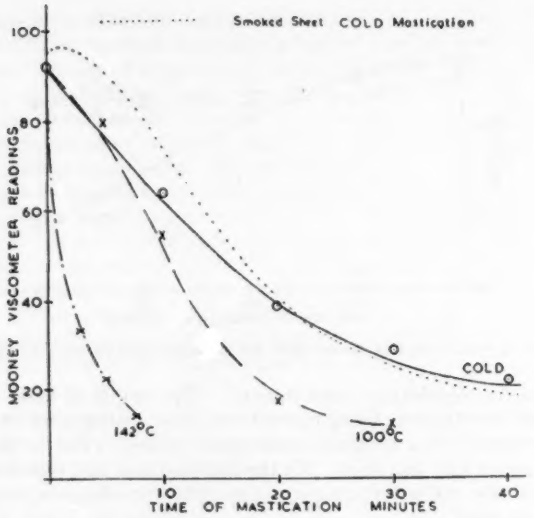

FIG. 5.—Mastication of smoked sheet + *o-o'*-dibenzamidodiphenyl disulfide in air.

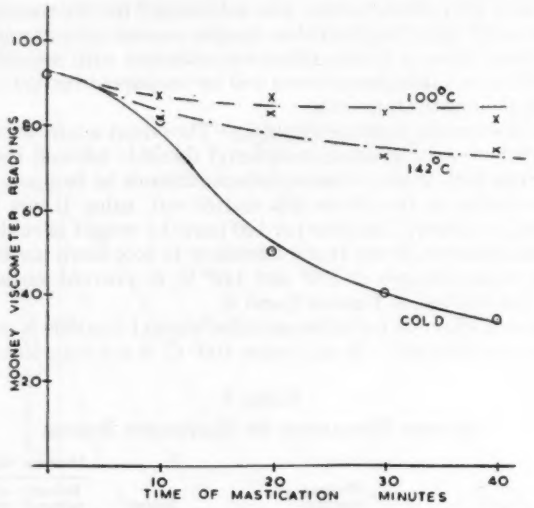

FIG. 6.—Mastication of smoked sheet and *o-o'*-dibenzamididiphenyl disulfide in nitrogen.

above 100°C more efficient than a corresponding amount of mercaptobenzothiazole. Its similarity under nitrogen is also very marked: only a slight breakdown at 100° and 142° C, but considerable breakdown in the cold; and it is evident that the mode of operation of these two compounds in assisting the breakdown of raw rubbers is the same.

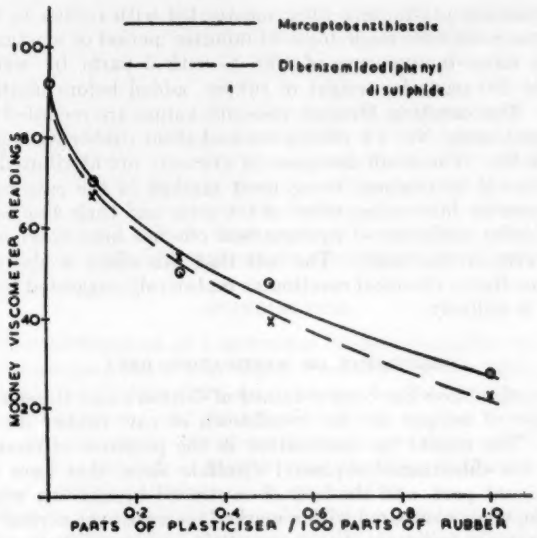

FIG. 7.—Chemical plasticization at 142° C in air. Effect of plasticizer concentration.

It was of interest to examine their relative effects as chemical plasticizers in air at concentrations below 1 part per 100 parts of rubber. Comparative data for air mastication for 5 minutes at 142° C is plotted in Figure 7. Efficiency of breakdown increases with increasing amounts of the plasticizer and below 0.5 parts per 100 parts of rubber there is no significant difference between them. However, it is claimed that *o-o'*-dibenzamidodiphenyl disulfide has only slight effect on the cure, whereas mercaptobenzothiazole, being in addition an accelerator of vulcanization, must be allowed for in subsequent compounding.

Effect of physical plasticizers on the mastication of smoked-sheet rubber in an oxygen-free atmosphere.—In view of the insignificant breakdown under nitrogen shown by compounds with give greatly increased breakdown in air at temperatures above 100° C, it was decided to examine the behavior of some of the more

TABLE 3

EFFECT OF PLASTICIZERS ON SMOKED-SHEET RUBBER MASTICATED IN NITROGEN
Mooney Viscosity of Original Sheet 97 to 98

Plasticizer	Mooney viscometer readings	Plasticizer	Mooney viscometer readings
Stearic acid	85.5	Pine oil	94.0
Zinc laurate	83.0		
Mineral oil	90.0	*Plastogen	91.0
Tricresyl phosphate	93.0	†Bondogen	91.0
Dibutyl phthalate	91.0		
Rosin oil	92.0		

* Plastogen—1.6 per cent sulfonated petroleum product in mineral oil.
† Bondogen—75 per cent sulfonated petroleum product in butyl alcohol.

common commercial plasticizers when masticated with rubber in the absence of air. Comparisons were made for a 20 minutes' period of mastication under nitrogen at a mixer-temperature of 100° C with 3 parts by weight of the compound per 100 parts by weight of rubber, added before mastication was commenced. The resulting Mooney viscosity values are recorded in Table 3, the rubber used being No. 1X ribbed smoked sheet rubber having a Mooney value of 97 to 98. The small decreases in viscosity are attributed to varying degrees of internal lubrication, being most marked in the case of fatty acid types. The greater lubricating effect of fat acids and their zinc salts as compared with similar additions of hydrocarbon oils has been commented on by previous workers in this field[5]. The fact that this effect is also observed in nitrogen means that a chemical reaction as tentatively suggested by Busse and Cunningham is unlikely.

DISCUSSION OF MASTICATION DATA

Further confirmation has been obtained of Cotton's and Busse's findings on the importance of oxygen for the breakdown of raw rubber during normal mastication. The results for mastication in the presence of mercaptobenzothiazole and *o-o'*-dibenzamidodiphenyl disulfide show that here too oxygen plays a prominent part, and the lack of continued breakdown when working under nitrogen, when compared with a marked increase over normal breakdown when working in air, indicates that the peptizing action of these compounds is due to their ability to increase the rate or efficiency of oxidative breakdown of the rubber molecule. In fact, the term chemical plasticizer in contradistinction to physical plasticizer referred to in Table 3, should be used in place of peptizer.

At the moment no really satisfactory explanation can be brought forward to account for the breakdown which takes place under nitrogen in the cold in the presence of these compounds. It may be pointed out that in nitrogen the breakdown with or without chemical plasticizers is insignificant at 100° and 142° C, but exists to a greater or lesser extent in the cold. These latter effects suggest that trapped air may not escape at the lower temperature and is sufficient to produce breakdown, which is greater in efficiency in the presence of an oxidative catalyst even at temperatures around 50° C.

Mastication of smoked-sheet rubber under nitrogen at 100° C, where no breakdown took place and any trapped air should have been displaced, followed by cooling, addition of mercaptobenzothiazole, and continued mastication in the cold under nitrogen, was carried out in an attempt to substantiate this theory. However, breakdown was obtained of the same order as observed by direct cold mastication of smoked sheet rubber with mercaptobenzothiazole under nitrogen.

At this stage the results and observations recorded above do not provide any definite answer to the question as to whether breakdown of rubber during mastication is a mechanical as well as an oxidative process. Although most of the evidence points to the latter, and establishes its role in the presence of chemical plasticizer, the greater breakdown in the cold than at 100° C during normal air mastication, and the breakdown observed in the cold under nitrogen in the presence of mercaptobenzothiazole and *o-o'*-dibenzamidodiphenyl disulfide, suggest some parallel mechanism of a different character.

PROPERTIES OF PURE-GUM VULCANIZATES COMPOUNDED IN AN OXYGEN-FREE ATMOSPHERE

INTRODUCTION

The observation of the almost complete lack of breakdown of raw rubber when masticating under nitrogen, as recorded in the first part of this paper, suggested the possibility of producing vulcanizable materials without appreciably reducing the molecular weight of the rubber employed. Comparison of the physical properties of the resulting vulcanizates with those of normal air-compounded materials would then provide information on variations of physical properties with stock viscosity in a range not previously investigated.

EXPERIMENTAL

During the development of a technique for the production of compounded stocks under nitrogen, where only slight breakdown of the rubber takes place it was observed that (1) complete compounding in the cold was not successful as the lack of breakdown, and the absence of any marked thermal softening, resulted in a poor dispersion of the vulcanizing ingredients, and (2) compounding at 100° C often resulted in considerable scorching of the stock, even with low sulfur and a delayed-action type of acceleration.

The method finally adopted was to add all the compounding ingredients with the exception of sulfur and to masticate at 100° C under nitrogen for 10 minutes. The machine was then stopped and cold water circulated through the blades and rotor for 5 minutes, during which time the sulfur was added through an opening in the top plate. After sweeping out again with nitrogen, mastication was continued for a further 5 minutes, the temperature of the stock being controlled by use of water or steam as desired, to ensure dispersion of the sulfur without any prevulcanization of the compound.

With many of the nitrogen-compounded stocks, it was found that, in attempting to produce a smooth press-cured sheet for physical testing, considerable curing occurred before sufficient flow had taken place to fill the mold. The resulting sample showed marked shrinkage on removal from the mold, had an uneven surface, and was of little value for testing purposes. The effect was overcome almost entirely by pressing out the compounded rubber under a cold press to as thin a sheet as possible, immediately on removal from the mixer, and allowing it to cool down in that condition. Shrinkage took place on removal from the press, but flat sections could be cut for molding purposes. These showed only very slight contraction after vulcanization, had a good smooth surface, and gave reproducible results in testing. All samples were press-cured

TABLE 4

COLD MASTICATION OF SMOKED-SHEET RUBBER + MERCAPTOBENZOTHIAZOLE IN AIR AND IN NITROGEN. PHYSICAL PROPERTIES OF VULCANIZATES

Composition	
Smoked-sheet rubber	100
Zinc oxide	5
Sulfur	3
Stearic acid	1
Mercaptobenzothiazole	1

Atmosphere	Mooney viscometer reading	Time of cure at 142° C (min.)	Tensile strength (kg. per sq. cm.)	Elongation at break %	Modulus at 500% E. (kg. per sq. cm.)
Air	73	10	232	830	32
		20	222	810	35
		30	235	835	35
Nitrogen	70	10	219	790	35
		20	239	825	31
		30	218	815	29

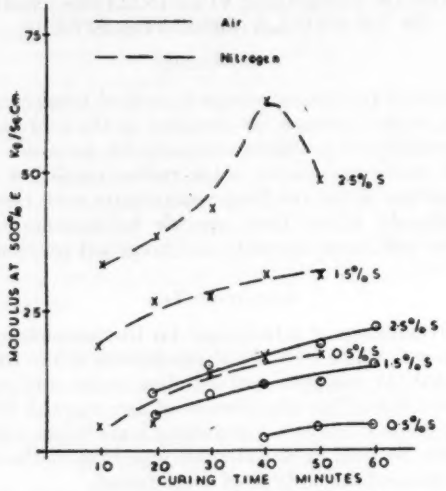

FIG. 8.—Benzothiazyl disulfide acceleration.

at 142° C (40 lb. per sq. in. steam pressure) to produce test-sheets 6 in × 6 in. × ¼ in.

COMPOUND DATA AND RESULTS

Cold breakdown in air and in nitrogen.—In view of the breakdown observed during mastication under nitrogen in the cold in the presence of mercaptobenzothiazole, it was decided to compare the physical properties after vulcanization of two identical pure-gum compounds, one with breakdown of the rubber as above, and one with normal cold breakdown in air, to give a similar stock plasticity in each case. For nitrogen compounding, the rubber was masticated in the cold under nitrogen with the mercaptobenzothiazole for 30 minutes, the remainder of the compounding ingredients added, and a further 10 minutes' period of mastication under nitrogen allowed for dispersion. For air compounding, the rubber with the mercaptobenzothiazole was masticated in air for 7 minutes in the cold, and after adding the compounding ingredients, masticated under nitrogen for a further 10 minutes. Compound formulation and physical test results are given in Table 4, from which it is evident that the physical properties of the resulting vulcanizates are very similar.

Benzothiazyl disulfide acceleration.—A series of compounds covering a range of sulfur contents was prepared under nitrogen by the method already detailed; and a similar series for comparison by air mastication in the mixer at 100° C for 5 minutes with all the compounding ingredients except the sulfur, followed by cooling and addition of sulfur and a further 5 minutes' mastication to bring the stock viscosity into the region of 50 Mooney. Details of the compositions are as follows:

Base composition		Compound	A	B	C	D	E
Smoked-sheet rubber	100	Parts of sulfur					
Zinc oxide	5	per 100 parts					
Stearic acid	1	of rubber	0.5	1.0	1.5	2.0	2.5
Benzothiazyl disulfide	0.5						

TABLE 5

BENZOTHIAZYL DISULFIDE ACCELERATION. TENSILE DATA

Compound	A		B		C		D		E	
	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
Tensile strength (kg. per sq. cm.)										
10 min. at 142° C	—	9	—	52	—	75	—	107	—	138
20 min. at 142° C	—	14	27	122	80	140	105	174	117	171
30 min. at 142° C	—	87	63	156	106	173	139	194	122	180
40 min. at 142° C	10	103	71	163	133	165	152	190	165	165
50 min. at 142° C	15	121	98	166	95	204	137	194	188	162
60 min. at 142° C	26		104		141		186		200	
Elongation at break (per cent)										
10 min. at 142° C	—	648	—	755	—	807	—	815	—	815
20 min. at 142° C	—	723	950	857	955	855	945	840	930	790
30 min. at 142° C	—	885	960	863	905	867	910	835	840	775
40 min. at 142° C	760	868	910	870	915	820	885	815	878	705
50 min. at 142° C	775	876	925	865	870	865	870	800	888	710
60 min. at 142° C	860		900		896		900		870	
Mooney viscosity of compounded stock	45	89	50	92	49.5	89	53	92.5	49.5	95

TABLE 6

PURE GUM COMPOSITIONS

Compound	F	G	H	J	K	L
Smoked-sheet rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	0.5	1	1	1	1	1
Sulfur	3.5	3.25	3	3	3	3
Mercaptobenzothiazole	0.5	—	—	—	—	—
Diphenylguanidine	—	1.25	—	0.5	—	—
N-Cyclohexyl-2-benzthiazole sulfenamide	—	—	0.5	0.5	0.5	0.5
Tetramethylthiuram disulfide	—	—	—	—	0.1	0.2

Comparison of these compounds by plotting the modulus at 500 per cent elongation against the time of cure is shown in Figure 8. The increase in modulus obtained by reducing the breakdown is maintained over the range from low to normal sulfur content. The data given in Table 5 show that, even with an abnormally low sulfur and low acceleration, an appreciable tensile strength is realized. The differences in the values at the shorter cure times are of considerable interest.

Normal and boosted acceleration.—A number of pure-gum compounds were examined, covering a range from very low to very high modulus type acceleration. *N*-Cyclohexyl-2-benzothiazole sulfenamide was used as a basis for all the boosted accelerator combinations, as it was found that its delayed-action effect was sufficient to allow safety in processing and good results in molding. Compositions are shown in Table 6. Plots of modulus at 500 per cent elongation against time of cure are shown in Figures 9, 10, and 11. With mercaptobenzothiazole and diphenylguanidine acceleration, a considerable increase in modulus is produced by preventing breakdown of the compounded stock; but with the boosted high modulus types this increase is no longer apparent. The

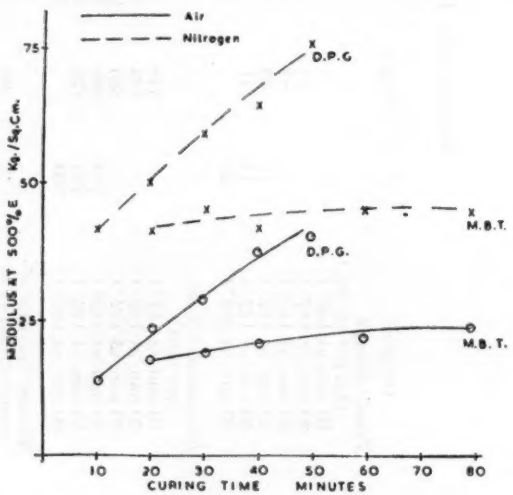

FIG. 9.—Mercaptobenzothiazole and diphenylguanidine acceleration.

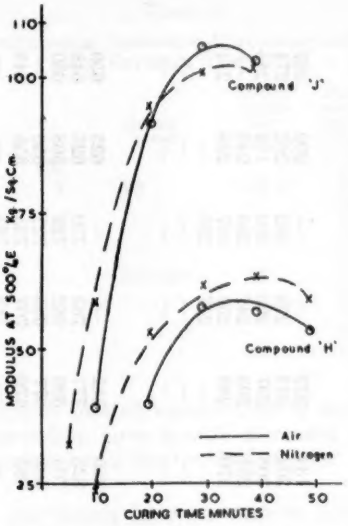

FIG. 10.—High modulus acceleration.

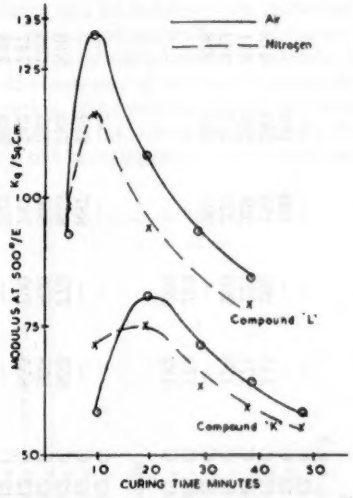

FIG. 11.—High modulus acceleration.

data in Table 7 are of interest in showing the difference in tensile strength given by air and nitrogen compounding.

Tetramethylthiuram disulfide vulcanization.—A pure-gum compound vulcanized with tetramethylthiuram disulfide was similarly investigated; the composition and physical data obtained are given in Table 8 and the modulus at

TABLE 7

PURE-GUM COMPOSITIONS. TENSILE DATA

Compound	F		G		H		J		K		L	
	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
Tensile strength (kg. per sq. cm.)												
5 min. at 142° C	—	—	—	—	—	—	134	222	—	—	209	267
10 min. at 142° C	—	—	130	188	—	196	304	313	296	332	262	274
20 min. at 142° C	145	201	199	233	318	323	308	297	266	306	194	245
30 min. at 142° C	171	221	228	256	311	313	281	293	247	284	246	—
40 min. at 142° C	176	203	226	262	282	293	270	288	257	267	238	211
50 min. at 142° C	—	—	201	255	276	278	—	—	247	276	—	—
60 min. at 142° C	179	213	—	—	—	—	—	—	—	—	—	—
80 min. at 142° C	182	206	—	—	—	—	—	—	—	—	—	—
Elongation at break (per cent)												
5 min. at 142° C	—	—	—	—	—	—	860	812	—	—	625	650
10 min. at 142° C	—	—	887	792	—	882	823	777	765	750	625	648
20 min. at 142° C	853	773	855	782	810	792	705	690	682	722	568	650
30 min. at 142° C	858	800	840	753	765	760	663	677	695	727	650	—
40 min. at 142° C	855	790	787	742	747	742	657	670	707	735	655	643
50 min. at 142° C	—	—	792	703	748	732	—	—	713	745	—	—
60 min. at 142° C	845	792	—	—	—	—	—	—	—	—	—	—
80 min. at 142° C	858	798	—	—	—	—	—	—	—	—	—	—
Mooney viscosity of compounded stock	53	91	58	95	50	83	45	75	44	77	51	Precured in Mooney

TABLE 8

TETRAMETHYLTHIURAM DISULFIDE VULCANIZATION COMPOSITION AND PHYSICAL TEST DATA

Composition		Atmosphere	Mooney viscometer reading	Time of cure at 142° C (min.)	Tensile strength (kg. per sq. cm.)	Elongation at break (%)
Smoked-sheet rubber	100					
Zinc oxide	2	Air	48.5	10	142	883
Tetramethylthiuram disulfide	3			20	162	817
				30	175	793
				40	179	775
				50	201	783
		Nitrogen	92	10	206	793
				20	248	777
				30	246	760
				40	257	742
				50	239	727

500 per cent elongation is plotted against time of cure in Figure 12. Here again nitrogen compounding gives greatly increased modulus, and the full tensile strength is developed in a shorter time of cure.

DISCUSSION OF COMPOUNDING DATA

It is evident from the results that with some types of pure-gum compounding, particularly those giving low or medium modulus vulcanizates, a considerable increase in modulus can be achieved by reducing the breakdown of the rubber to a minimum during compounding. However, as the acceleration is modified to give high-modulus vulcanizates, a marked decrease in the sensitivity of the modulus to the viscosity of the uncompounded stock takes place; and, with considerable boosting, the modulus cannot be further increased by reducing breakdown of the rubber. It is proposed to apply the technique of nitrogen compounding to carry out investigation over a wide range of stock plasticity,

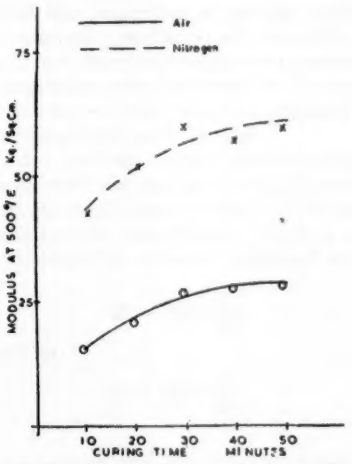

FIG. 12.—Tetramethylthiuram disulfide vulcanization.

and it will be of interest to determine how far the above conclusions are borne out, both with pure-gum types and with compounds containing fillers.

SUMMARY

Confirmation has been obtained that raw rubber when masticated in the absence of oxygen undergoes only a limited amount of breakdown; and it has been shown that two of the better known socalled "peptizers" or chemical plasticizers of rubber, *viz.*, mercaptobenzothiazole and *o-o'*-dibenzamidodiphenyl disulfide, require oxygen to be effective.

A range of pure-gum rubbers has been compounded under nitrogen, and the physical properties after vulcanization compared with corresponding air-compounded rubbers. Some types of acceleration give vulcanizates whose physical properties are very sensitive to changes in the viscosity of the unvulcanized stock, decrease in viscosity giving decreased modulus. Other types of acceleration, notably "boosted" combinations which give high modulus vulcanization, are insensitive to stock viscosity changes over a wide range.

This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association.

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INVESTIGATIONS IN THE FIELD OF RUBBER VULCANIZATION. VI. CHANGE IN TWO-DIMENSIONAL EXTENSION MODULUS DURING VULCANIZATION OF NATURAL AND BUTADIENE-STYRENE RUBBERS

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In the preceding communications of this series[1], it was shown that the vulcanization of rubber is accompanied by the mutual superimposition of a number of processes, among which some are constructive, *i.e.*, favor an increase in the size of molecular structures and their mutual combination, while others are destructive, *i.e.*, lead to a disintegration of molecular structures. In the case of natural rubber, the latter processes are connected principally with the action of molecular oxygen. This point of view made it possible to explain[2] the phenomenon of vulcanization optimum for natural-rubber mixtures containing small percentages of sulfur. In the case of butadiene polymers, whose structure approaches more closely the 2–1 type, it was shown by Dogadkin[3] that the action of oxygen is constructive even in the early stages of oxidation, inasmuch as, in the presence of a relatively undeveloped process of disintegration of the main chains of the polymer, local intermolecular bonds and bonds possessing a chemical character appear in the oxidation products. Because of this characteristic property of butadiene polymers, the kinetics of the change of their physico-chemical properties during vulcanization differ in many ways from the kinetics of the change of the properties of natural rubber. With respect to certain properties, for example, swelling and solubility, the phenomenon of vulcanization optimum is not observed to apply to butadiene polymers. While, with respect to other properties, the phenomenon of vulcanization optimum is observed, it must be explained on the basis of a different mechanism, which is discussed in the work of Dogadkin and Karmin[4].

In connection with the problem under consideration, undoubted interest attached to an investigation of the change during the vulcanization of various types of rubber of some physical characteristic which would represent a well defined function of constructive phenomena. Such a characteristic may be found in the modulus of elasticity, which is expressed as:

$$E = 7RT\frac{\rho}{M} \tag{1}$$

according to Kuhn[5], and as:

$$E = 3RT\frac{\rho}{M} \tag{2}$$

according to Wall[6].

* Translated for Rubber Chemistry and Technology from the *Kolloidnyi Zhurnal* (*Colloid Journal*), *U.S.S.R.* Vol. 10, No. 2, pages 94–102, March–April 1948, by Alexander Bogrow, Cambridge, Mass.

However, the determination of a modulus of high elasticity during linear deformation causes great difficulties, which result from the necessity of obtaining data in equilibrium states. It is more convenient to determine the analogous constant for two-dimensional extension, which, according to Treloar[7], has the following form:

$$G = NkT \tag{3}$$

where G is the elasticity constant (modulus) during two-dimensional extension; N is the number of sections (molecular chains) between sites of the vulcanizate lattice; k is Boltzmann's constant; and T is the absolute temperature. Thus, by making use of Equation (3), a determination of the elasticity constant (modulus) for two-dimensional extension should make it possible to follow the progress of constructive and destructive processes (increase and decrease in the number of sites in the vulcanizate lattice), as well as to analyze the reasons for the varying behavior of different rubbers during the process of their vulcanization.

EXPERIMENTAL PROCEDURE

As previously shown by the authors[8], the extent of plastic deformation during two-dimensional extension is considerably smaller than during linear elongation. Generally speaking, this makes it possible to apply the method of two-dimensional extension to mixtures in the initial stage of vulcanization,

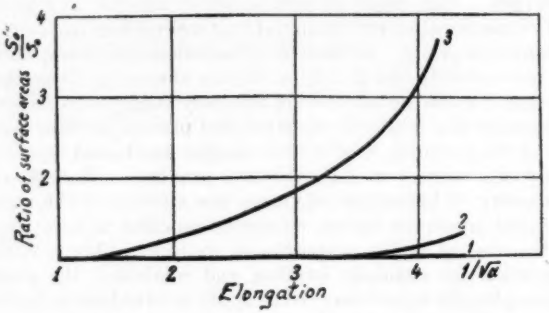

FIG. 1.—Residual deformation as function of total linear deformation for mixtures with different sulfur contents 1: 2.80%; 2: 1.18%; 3: 0.70%.

thus to make possible a more extensive study of this phenomenon. However, even in the case of two-dimensional extension, mixtures with low degrees of vulcanization show appreciable residual deformations (Figure 1). For this reason, in calculating the elasticity constant, the elastic deformation was in each case determined as the difference between total and residual deformation.

The numerical value of two-dimensional extension was determined with the aid of an apparatus described elsewhere[8]. This apparatus makes it possible to determine the height h and the radius a of a spherical segment formed by a film of vulcanizate blown up by an air pressure p, which is measured by means of a liquid manometer. The numerical value of deformation was determined as the ratio of the thickness d of the deformed film to its initial thickness d_0:

$$\alpha = \frac{d}{d_0} \tag{4}$$

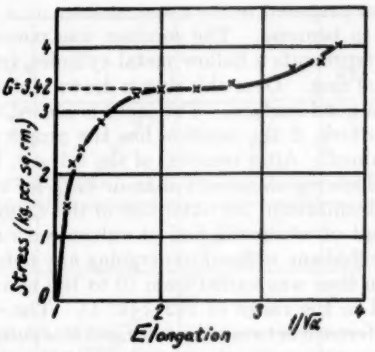

FIG. 2.—Stress as function of extension in two-dimensional deformation. Broken line marks value of elasticity constant (G).

This quantity α is connected with the measured quantities a and h by the following equation:

$$\alpha = \frac{a^2}{a^2 + h^2} \tag{5}$$

The stress t, based on a unit length of film circumference, and corresponding to the deformation α, is calculated from the following formula:

$$t = \frac{p(a^2 + h^2)}{4d_0h} \tag{6}$$

According to Treloar:

$$t = G(1 - \alpha^3) \tag{7}$$

from which the value of the two-dimensional extension modulus is easily determined for the case of $\alpha = 0$. In connection with this, the experimental data are used to plot a curve representing stress as a function of the extension of the film. Since it is assumed that the deformation of the film is not accompanied by a change in its volume, the following correlation between the film extension α' and the compression α is derived:

$$\alpha' = \frac{1}{\sqrt{\alpha}} \tag{8}$$

Figure 2 shows a typical experimental curve, plotted in the above-mentioned coördinate system (stress t *vs.* extension α'), for a natural-rubber vulcanizate containing 1.85 per cent of sulfur. This curve has a horizontal section, the continuation of which to the stress axis marks on the latter a value which equals the elasticity constant G.

Two mixtures of compositions A and B were subjected to vulcanization.

	Parts by weight
A. Smoked sheet	100
Sulfur	2
Zinc oxide	5
Stearic acid	2
Mercaptobenzothiazole	0.6
B. Buna-S	100
Sulfur	3
Zinc stearate	2
Mercaptobenzothiazole	1

The mixtures were prepared in the usual manner on a roll mill, after which they were dissolved in benzene. The solution was poured into special small molds. Each mold represents a hollow metal cylinder, into the base of which is inserted a flat metal ring. Over this ring is drawn a sheet of wet cellophane, which dries to give a good surface. The mold is placed on a horizontal glass base, as a result of which, if the solution has the proper viscosity, a uniform film thickness is attained. After removal of the solvent, the ring was inserted into a special case, which was immersed in an oil bath for vulcanization. After completion of the vulcanization, the outer side of the cellophane was moistened with water, as a result of which the film of vulcanized rubber could be easily detached from the cellophane without undergoing any deformation.

The vulcanization time was varied from 10 to 160 minutes. The temperature was maintained in the range of 142–144° C. The combined sulfur was determined as the difference between the total and free sulfur in the vulcanizate. The tensile strength was determined with a Smirnov dynamometer.

EXPERIMENTAL DATA

CHANGE IN TWO-DIMENSIONAL EXTENSION MODULUS

Figure 3 shows two-dimensional deformation curves for Buna-S vulcanizates of different degrees of vulcanization. By applying the method described above to these curves, it was possible to calculate the values of the two-dimensional extension modulus.

Figure 4 shows these moduli as a function of vulcanization time, together with curves describing the kinetics of sulfur addition and curves indicating the changes in tensile strength and relative elongation.

Figure 5 shows analogous curves for natural-rubber mixtures. The appearance of the curves showing the changes in modulus and relative elongation demonstrates the distinction between natural-rubber mixtures and mixtures based on butadiene-styrene rubber. This distinction becomes particularly clearly pronounced on inspection of the correlation between the modulus G and the quantity of combined sulfur in the vulcanizates (Figures 6 and 7). In natural-rubber mixtures, the elasticity constant increases with the percentage of combined sulfur until the vulcanization optimum is reached; thereupon, in spite of the still continuing increase in combined sufur, the modulus drops off sharply. In mixtures based on butadiene-styrene rubber, the curve describing the change in the two-dimensional extension modulus has a more complex form; some time after the instant of optimum vulcanization (as measured by the change in strength), the modulus experiences another sharp rise.

In our opinion, such a distinction in the character of the change of the two-dimensional extension modulus is in full agreement with the views relating to the mechanism of the phenomenon of vulcanization optimum developed by us[1]. In conformity with Equation (3), the modulus is a linear function of the number of cross-linkages formed between molecular chains during vulcanization; it is to be expected that this constant must grow as more sulfur combines with the rubber, inasmuch as the sulfur links together the molecular chains of the rubber. The decreasing modulus in natural-rubber mixtures after the instant of optimum vulcanization (while the addition of sulfur still continues) is the result of the destructive action of molecular oxygen (or possibly of some other factor as well). As already pointed out, in mixtures based on butadiene-styrene rubber, oxygen acts as a constructive factor in a certain stage of the process. For this reason, the cross-linkage of molecular chains in such mixtures

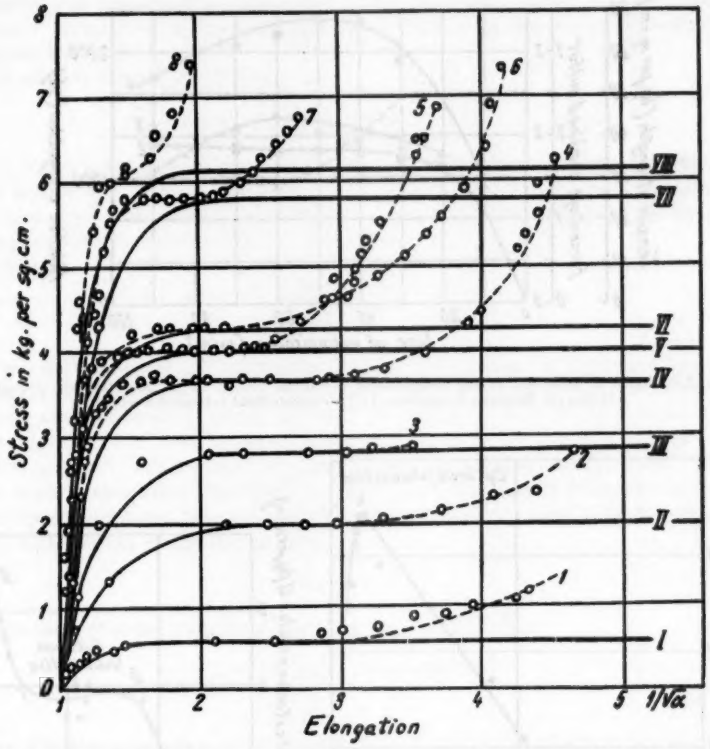

FIG. 3.—Stress as function of extension during two-dimensional deformation of vulcanizates with different sulfur contents. 1: 0.70%; 2: 0.96%; 3: 1.10%; 4: 1.18%; 5: 1.74%; 6: 2.64%; 7: 2.74%; 8: 2.80%. ----- Experimental curves. ——— Theoretical curves.

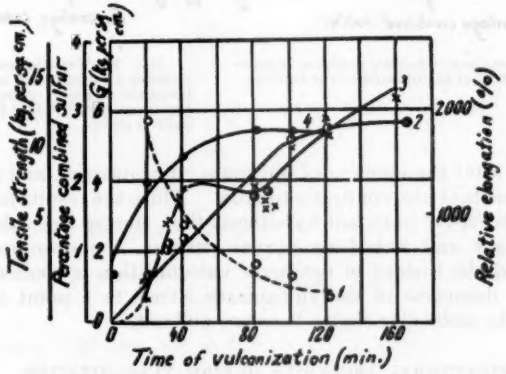

FIG. 4.—Change in properties during vulcanization of butadiene-styrene rubber. 1: Relative elongation; 2: Sulfur addition; 3: Two-dimensional extension modulus; 4: Tensile strength.

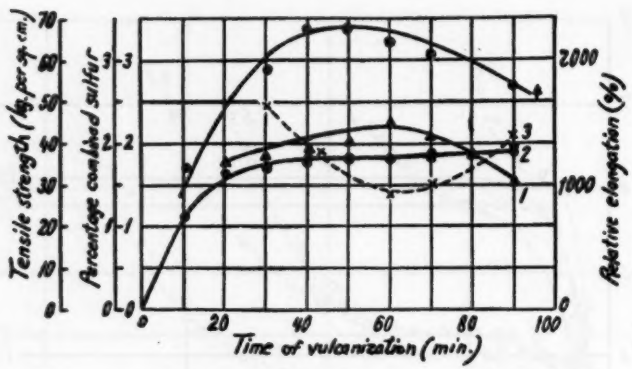

FIG. 5.—Change in properties during vulcanization of natural rubber. 1: Tensile strength; 2: Sulfur addition; 3: Relative elongation; 4: Two-dimensional extension modulus.

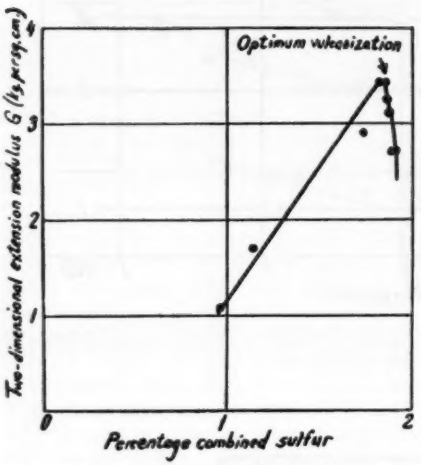

FIG. 6.—Two-dimensional extension modulus as function of sulfur content of natural-rubber vulcanizates.

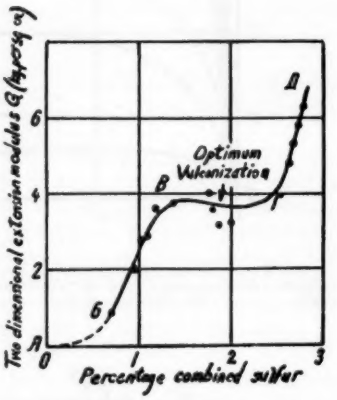

FIG. 7.—Two-dimensional extension modulus as function of sulfur content of butadiene-styrene rubber vulcanizates. Letters on curve: A B C D E (from left to right in order).

continues even after the moment of optimum vulcanization, and consequently the elasticity constant also continues to grow. Thus, the results presented here confirm the previously[9] proposed hypothesis that, during the vulcanization of butadiene rubbers and butadiene-styrene rubbers, the drop in mechanical strength beyond the instant of optimum vulcanization is connected with an increase in the denseness of the vulcanizate lattice to a point at which the orientation of the molecular chains becomes difficult.

STRUCTURAL PROCESSES DURING VULCANIZATION

The peculiar character of the variation of the two-dimensional extension modulus G as a function of the content of combined sulfur in the vulcanizate is

a reflection of the structural processes occurring in the rubber during vulcanization. An analysis of these changes may be based on the theory of elasticity proposed by Wall.

As already stated previously[2]:

$$G = NkT$$

where N is the number of molecular chains, *i.e.*, of sections between sites in the space lattice of 1 cc. of vulcanizate. It is easily realized that the formation of each new site in an already existing lattice increases the number of molecular chains (sections between sites) by two units.

Thus:

$$\frac{dN}{dn} = 2 \tag{9}$$

where n is the number of sites in the lattice. Let it now be assumed that the free sulfur in the mixture subjected to vulcanization is uniformly distributed, and the sites between the chains are each filled by one atom of sulfur (monosulfide bridges). As shown by experiments on the interaction of vulcanizates with methyl iodide[10], this assumption closely approaches the actual facts. The same experiments show that there is a direct proportionality between the total quantity of combined sulfur S and that part of it which goes to fill the lattice sites (monosulfide bridge sulfur S_m):

$$S_m = \gamma \cdot S \tag{10}$$

On the basis of these considerations, it is possible to write:

$$S = \frac{S_m}{\gamma} = \frac{n \cdot m \cdot 100}{\rho \cdot \gamma} \tag{11}$$

where S is the percentage of combined sulfur; n is the number of monosulfide bridges in 1 cc. of vulcanizate; m is the atomic weight of sulfur; and ρ is the density of the vulcanizate.

To find the correlation between the elasticity constant G and the quantity of combined sulfur S, use is made of the following equation:

$$\frac{dG}{dS} = \frac{dG}{dn} \cdot \frac{dn}{dS} \tag{12}$$

Differentiation of Equation (3) with substitution according to (9) gives:

$$\frac{dG}{dn} = 2kT \tag{13}$$

Differentiation of Equation (11) gives:

$$\frac{dn}{dS} = \frac{\rho \cdot \gamma}{m \cdot 100} \tag{14}$$

Substitution of (13) and (14) in Equation (12) yields:

$$\frac{dG}{dS} = \frac{2kT\rho\gamma}{m \cdot 100} \tag{15}$$

Assuming $T = 293°$ K, $\rho = 0.94$, and substituting the values of k and m, the following final expression is obtained:

$$\frac{dG}{dS} = \gamma \cdot \frac{1.36 \cdot 10^{-16} \cdot 293 \cdot 0.94 \cdot 6.02 \cdot 10^{23}}{32 \cdot 100}$$

$$= 14.1 \cdot 10^{6}\gamma \text{ dynes per sq. cm.} = 14.4\gamma \text{ kg. per sq. cm.} \qquad (16)$$

In accordance with the above expression, the two-dimensional extension modulus must vary with the percentage of combined sulfur in conformity with a linear law. In actual fact, a more complex correlation is observed. However, the deviation from the linear relationship finds a rational explanation. The raw mixture is a plastic material, for which $G = 0$ (Point A in the origin of the coördinate system, Figure 7). In the initial stage of vulcanization, linkage of molecular chains occurs, and this brings about an increase in the elasticity constant (Segment AB, drawn in as a broken curve). In this stage, the molecular chains are not yet linked together to form a single space lattice, and the elasticity constant does not vary linearly. Point B apparently corresponds to the instant in which the formation of the space lattice of the vulcanizate is completed; subsequent addition of sulfur increases the denseness of this lattice, in conformity with the mechanism analyzed above. For this reason, the segment of the experimental curve following Point B is rectilinear, as defined by Equation (16).

In mixtures based on natural rubber, the rectilinear segment of the curve representing the two-dimensional extension modulus continues until the instant of optimum vulcanization is reached; in mixtures based on butadiene-styrene rubber, the straight-line segment begins to curve somewhat sooner (Point C). This new deviation from linearity is explained in the case of natural-rubber mixtures by the oxidative destruction of the space lattice of the vulcanizate[11]. In mixtures based on butadiene-styrene rubber, the destructive process is less pronounced; more than that, in such mixtures the curve segment reflecting the tendency toward a diminution of the modulus (Segment CD) is followed by a new rise, during which the elasticity constant increases linearly. This second rectilinear segment reflects certain processes which lead to the mutual linkage of the molecular chains; these processes are connected principally with the action of heat and oxygen upon the butadiene-styrene rubber.

Making use of Equation (16), the slope of the rectilinear segments may serve as a basis for determining the value of the coefficient γ, which expresses the quantity of bridge sulfur S_m as a fraction of the total quantity of combined sulfur S. For a natural-rubber vulcanizate, $\gamma = 0.19$. This number may be compared with that obtained by determining the monosulfide bridge sulfur in the vulcanizate by the methyl iodide method[12]. In a natural-rubber vulcanizate containing 7 per cent of total sulfur, the monosulfide bridge sulfur S_m constitutes 15 per cent of the total combined sulfur s[10]. According to data of Selker and Kemp[13], in mixtures containing 3 per cent of total sulfur, monosulfide bridge sulfur constitutes 35.8 per cent. If the average value of S_m, which equals 21 per cent, is taken (corresponding to $\gamma = 0.21$), the agreement between the values of γ obtained by methods that are so different must be admitted to be satisfactory.

In mixtures based on butadiene-styrene rubber, the monosulfide bridge sulfur S_m, as determined by the methyl iodide method in a mixture containing 3 per cent sulfur, constitutes 22.5 per cent of the total combined sulfur. This quantity is considerably smaller than that corresponding to the coefficient γ,

as determined from the two-dimensional deformation modulus ($\gamma = 0.76$ for the segment DE). Such a discrepancy may be explained by the fact that, during the vulcanization of butadiene-styrene rubber, cross-linkages between the chains are formed not only by sulfur, but also by molecular oxygen, as well as, possibly, by the direct action of heat. It is evident that the two-dimensional deformation modulus reflects all types of cross-linkages, whereas only monosulfide linkages can be determined by the methyl iodide method. For this reason, in vulcanizates based on types of rubber, in which oxygen plays the part of a constructive factor, the value of the coefficient γ, as determined from Equation (16), must always be higher than the quantity obtained from determinations by the methyl iodide method.

CONCLUSIONS

1. The change in the modulus of two-dimensional extension during the vulcanization of natural and butadiene-styrene rubber has been investigated.

2. In natural-rubber vulcanizates, the two-dimensional extension modulus varies with the percentage of combined sulfur along a curve which possesses a maximum; the ascending branch reflects processes of linkage between molecular chains, while the descending branch—after the vulcanization optimum—indicates the presence of processes of disintegration of the spatial structure.

3. In vulcanizates based on butadiene-styrene rubber, the descending branch is negligible in extent; it is immediately followed by a second rise in the modulus curve, which is connected principally with constructive processes brought about by the action of oxygen.

The following equation is proposed:

$$\frac{dG}{dS} = \frac{\gamma \cdot 2kT\rho}{m \cdot 100}$$

where γ is a coefficient which shows the ratio of monosulfide bridge sulfur to the total quantity of combined sulfur. For natural-rubber vulcanizates, the value of this coefficient ($\gamma = 0.19$) coincides with the value obtained in experiments on the determination of bridge sulfur by its reaction with methyl iodide ($\gamma = 0.21$).

5. In vulcanizates based on butadiene-styrene rubber, the quantity γ, as calculated from the above equation ($\gamma = 0.76$), is considerably higher than that calculated from data on the reaction with methyl iodide ($\gamma = 0.23$). This indicates that, in butadiene-styrene rubber, the linkage of molecular chains occurs both under the action of sulfur and as a result of thermooxidative processes.

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[11] As pointed out by Gol'berg, the above mentioned dependence of the modulus of elasticity during the constructive process on the percentage of combined sulfur can be derived from general statistical considerations. As a matter of fact, if the molecular-chain sections between two lattice sites contain n double bonds, of which l exist under favorable conditions from the point of view of activation energy and mutual proximity, the probability of chain linkage is given by the following expression:

$$p = \frac{l}{n} \tag{17}$$

If the linkage processes take place with the participation of S_m sulfur atoms among the total quantity of reacted atoms, the probability of the following inequality:

$$\left| \frac{S_m}{S} - p \right| < E \tag{18}$$

where E is any arbitrary small number, will approach unity if S is sufficiently large in comparison with S_m. On the basis of this inequality, it is possible to write the following approximate equation:

$$S_m = pS \tag{19}$$

which states that the quantity of bridge sulfur, and consequently, in conformity with Equation (3), also the modulus of elasticity, are linear functions of the total combined sulfur. This linear correlation, however, is valid only if, in agreement with the above inequality (18), the total quantity of sulfur S is large. If the quantity of reacting sulfur is small—a condition observed beyond the instant of optimum vulcanization—Equation (19) cannot be written, and this signifies that a linear correlation between S and G no longer exists.

[12] See Part V of this series of investigations.

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INVESTIGATIONS IN THE FIELD OF RUBBER VULCANIZATION. VII. INFLUENCE OF ORGANIC ACCELERATORS ON THE KINETICS OF VULCANIZATION AND THE PROPERTIES OF NATURAL-RUBBER VULCANIZATES *

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In the modern formulation of natural and synthetic rubber mixtures, widespread use is made of various organic substances which reduce the time required for vulcanization, and which have received the general designation of vulcanization accelerators. It has been pointed out that the action of vulcanization accelerators in natural-rubber mixtures consists, not only in reducing the time necessary for attaining optimum physico-mechanical properties, but also in improving these properties in comparison with those of vulcanizates containing no organic accelerators. Some time ago, one of the authors of the present communication[1] explained this phenomenon as a result of the diminished influence of destructive processes from the reduced vulcanization time. The previously proposed kinetic equation[2] for the vulcanization of natural-rubber mixtures containing small proportions of sulfur makes it possible to investigate the influence of accelerators on the varying parameters of the kinetic curve relating to the vulcanization process. A comparison of the results of such an investigation with variations in the character of the experimentally obtained kinetic curves for rubbers containing various organic accelerators opens the way for a systematic study of the mechanism which governs the intensifying action of organic vulcanization accelerators.

The kinetic equation of the change of tensile strength during vulcanization:

$$\pi = \pi_0[1 + a'S_0(1 - e^{-k_1\tau})][1 - b'O_0(1 - e^{k_2\tau})] \qquad (1)$$

contains four constants, which differ in the case of mixtures containing equal quantities of added sulfur S_0 and oxygen O_0 capable of reacting with rubber. These are, first of all, the rate constants of the addition of sulfur (k_1) and oxygen (k_2) to rubber and, secondly, the constants a' and b', which reflect the proportionality between the tensile strength of the vulcanizates and the quantities of sulfur and oxygen, respectively, combined with the rubber. These latter constants indicate the fractions of sulfur and oxygen utilized, respectively, to form local linkages between the rubber molecules or to destroy such linkages. In addition to π_0 (the mechanical strength of the raw mixture), the following parameters characterize the kinetic strength curves: (1) maximum strength at

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the vulcanization optimum, π_m; (2) time required to attain maximum strength, τ_m; (3) strength at the instant when this strength practically ceases to change (limiting or equilibrium strength) π_e; (4) time required to attain the limiting strength, τ_e (*cf.* Figures 1–4). These parameters are of the greatest importance in determining the technical properties of mixtures subjected to vulcanization.

The changes in the kinetic curves resulting from corresponding consecutive and separate changes in the values of the above-mentioned constants are shown in Figures 1–4. In this connection, it has been assumed that $\pi_0 = 10$; $S_0 = O_0 = 1$. An increase in the sulfur-addition rate constant k_1 results in a change in some of the parameters of the kinetic curve; the maximum strength π_m increases, while the time τ_m required to attain it decreases (Figure 1). The other parameters (the limiting strength π_e and the time τ_e required to attain it) remain unchanged. An increase in the oxygen-addition rate constant k_2 (Figure 2) results in a diminution of π_m and τ_m, as well as in a reduction of the time τ_e required to attain the limiting strength, whereas the limiting strength π_e itself remains unchanged, as in the first case. Changes in the constants a' and b' do not lead to any changes in the time parameters τ_m and τ_e of the resulting kinetic curves (Figures 3 and 4), but are reflected in changes of π_m and π_e. Thus, by investigating the physico-mechanical properties of vulcanizates, it is possible to estimate the influence of a given component of the mixture on the parameters of the kinetic strength curve.

Experimental data on the vulcanization of natural-rubber mixtures containing various organic accelerators show that practically all parameters of the

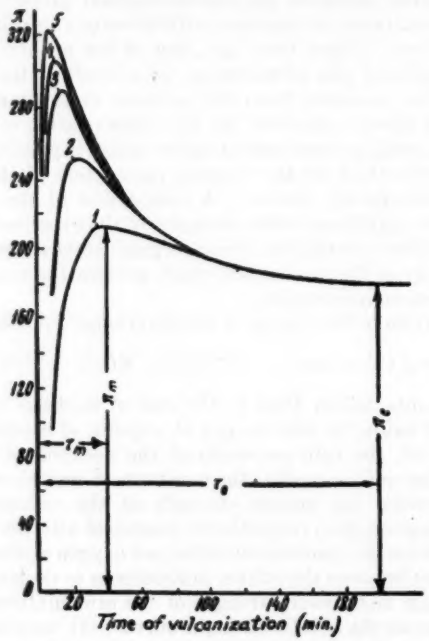

FIG. 1.—Change in kinetic vulcanization curves resulting from changes in constant k_1 ($\pi_0 = 10$; $k_2 = 0.025$; $a' = 35$; $b' = 0.5$). Each curve corresponds to definite value of k_1: (1) 0.05; (2) 0.10; (3) 0.20; (4) 0.30; (5) 0.50.

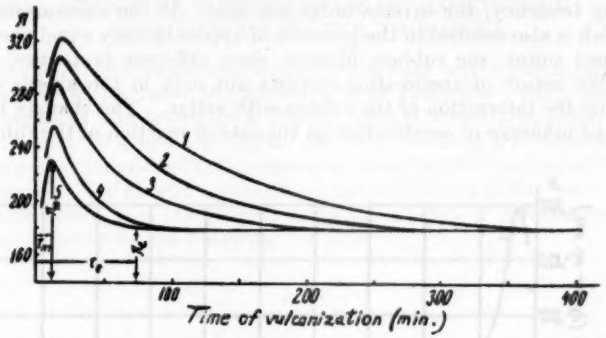

FIG. 2.—Change in kinetic vulcanization curves resulting from changes in constant k_2 ($\tau_0 = 10$; $k_1 = 0.2$; $a' = 35$; $b' = 0.5$). Each curve corresponds to definite value of k_2: (1) 0.010; (2) 0.015; (3) 0.025; (4) 0.050; (5) 0.075.

kinetic strength curve change as one accelerator is replaced by another. Thus, Figure 5 shows kinetic vulcanization curves for the following base mixture, treated with various accelerators: smoked sheet 100, sulfur 2, zinc oxide 5, and stearic acid 2 parts by weight. To this base mixture were added equimolecular quantities of the following accelerators: diphenylguanidine (DPG) 0.756 parts by weight (Mixture 3), mercaptobenzothiazole (Captax) 0.6 parts by weight (Mixture 2), and tetramethylthiuram disulfide (thiuram) 0.855 parts by weight (Mixture 1). At the conclusion of vulcanization, all three mixtures contain equal percentages of combined sulfur; yet their tensile strengths and swelling tendencies are different. The highest strength is exhibited by the rubber compounded with thiuram; this is followed by the rubber containing Captax, with the vulcanizate containing DPG possessing the least strength. With respect

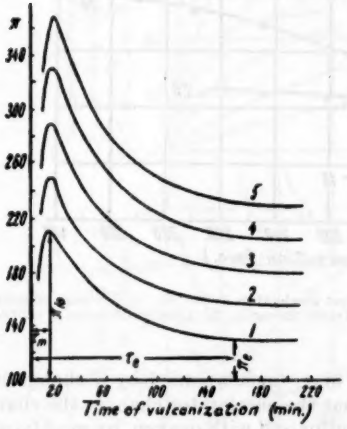

FIG. 3.—Change in kinetic vulcanization curves resulting from changes in constant a' ($\tau_0 = 10$; $k_1 = 0.2$; $k_2 = 0.025$; $b' = 0.5$). Each curve corresponds to definite value of a': (1) 25; (2) 30; (3) 35; (4) 40; (5) 45.

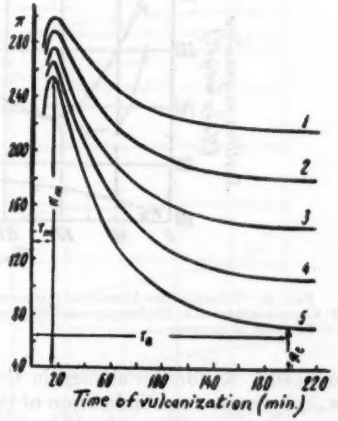

FIG. 4.—Change in kinetic vulcanization curves resulting from changes in constant b' ($\tau_0 = 10$; $k_1 = 0.2$; $k_2 = 0.025$; $a' = 35$). Each curve corresponds to definite value of b': (1) 0.4; (2) 0.5; (3) 0.6; (4) 0.7; (5) 0.8.

to swelling tendency, the inverse order prevails. At the vulcanization optimum, which is also reached in the presence of approximately equal percentages of combined sulfur, the rubbers likewise show different properties. Consequently, the action of accelerators consists not only in the kinetic effect of accelerating the interaction of the rubber with sulfur. The changes in τ_e also point to the influence of accelerators on the rate of reaction of the rubber with

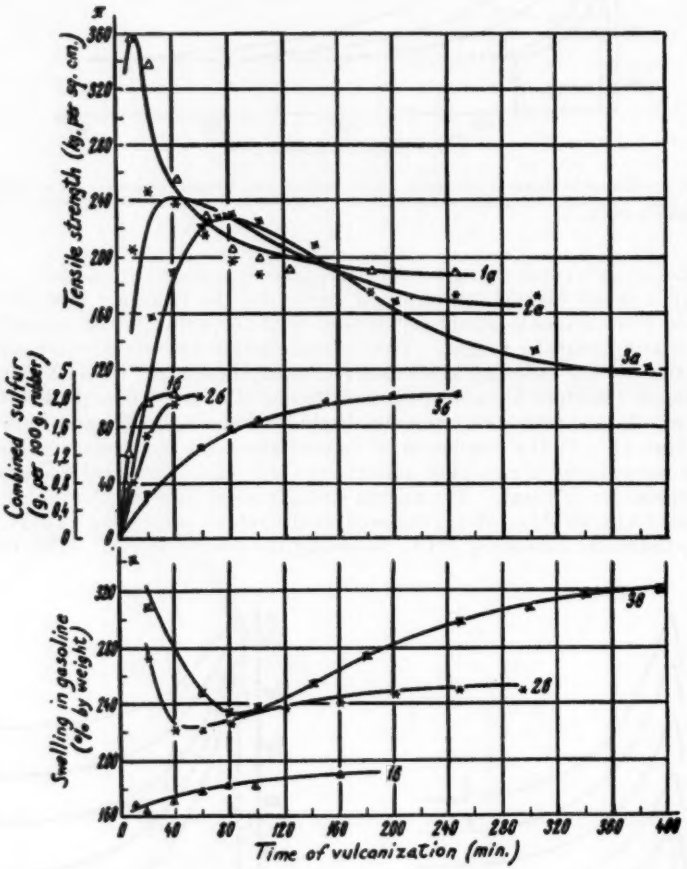

FIG. 5.—Vulcanization kinetics of mixtures with different accelerators at 143° C. 1: Thiuram mixture; 2: Captax mixture; 3: Diphenylguanidine mixture. (a) Tensile strength; (b) Addition of sulfur to rubber; (c) Swelling in benzene.

oxygen. As for the change in the values of π_e (accompanied by a change in π_m), it serves as an indication of the fact that the accelerator changes the character of the reactions of rubber, both with sulfur and with oxygen, by modifying the types of sulfur compounds and oxygenated compounds formed, which is in turn reflected (through the changed constants a' and b') in the mechanical and physical properties of the vulcanizate.

EFFECT OF ACCELERATORS ON KINETICS OF ADDITION OF SULFUR TO RUBBER

Figures 6, 7, and 8 summarize experimental data on the vulcanization of the above-mentioned mixtures at temperatures of 123°, 133°, 143°, and 153° C. Tensile strength was tested in a 200-kg. dynamometer, the lower clamp of which moved with a speed of 500 m. per min.; swelling was estimated by increase in weight; combined sulfur was determined by the method of Bolotnikov and Gurova[3]. The kinetic constants of the addition of sulfur were calculated on the assumption that the process obeys the kinetics of monomolecular reactions, as expressed by the following formula:

$$k_1 = \frac{6}{\tau} \tag{2}$$

where τ is the instant of practical completion of the reaction[4]. The kinetic constants of the process, obtained at four different temperatures, make it possible to calculate the apparent activation energy with the aid of Arrhenius's equation. At the same time, Equation (1) for the change in mechanical strength was used to calculate the constants k_1 of the constructive processes, which reflect the interaction between the rubber and sulfur, and the values obtained served as a basis for determining the apparent activation energy of

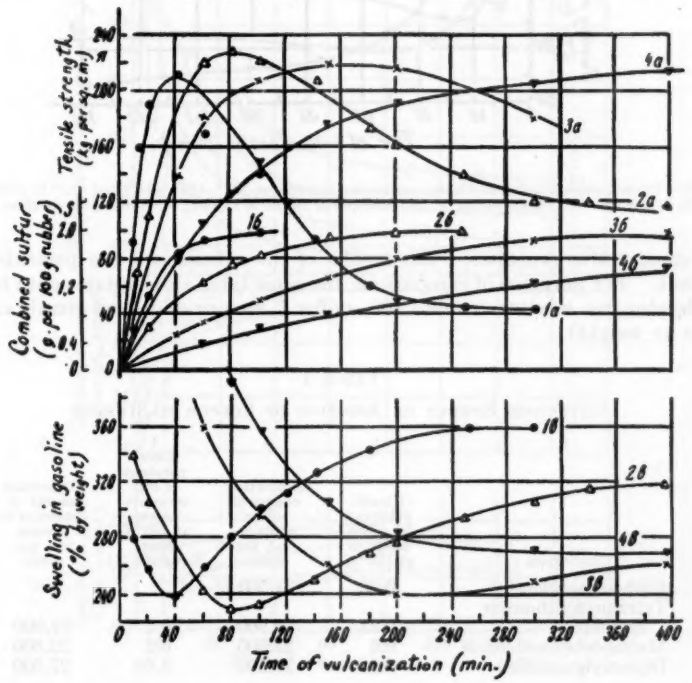

FIG. 6.—Vulcanization kinetics of diphenylguanidine-containing mixture at 123°, 133°, 143°, and 153°C (Curves 4, 3, 2, and 1). (a) Tensile strength; (b) Addition o sulfur to rubber; (c) Swelling in gasoline.

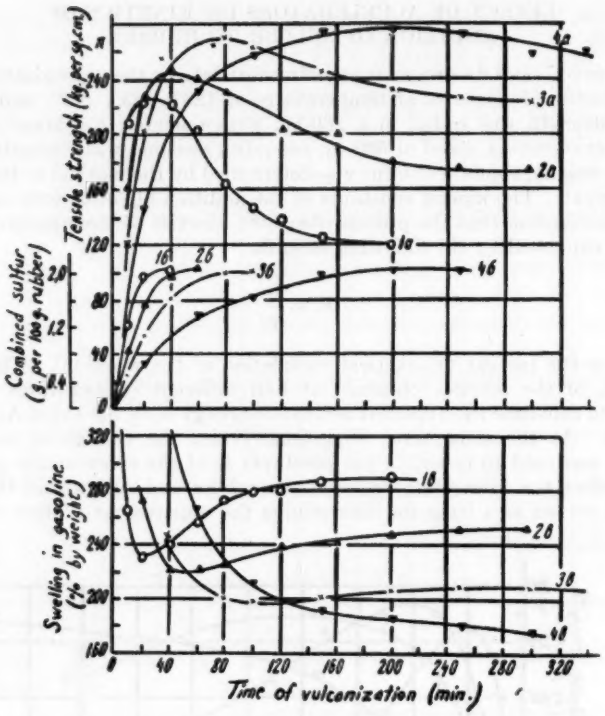

FIG. 7.—Vulcanization kinetics of Captax-containing mixture at 123°, 133°, 143°, and 153° C (Curves 4, 3, 2, and 1). (a) Tensile strength; (b) Addition of sulfur to rubber; (c) Swelling in gasoline.

the constructive processes. The results of the calculations are presented in Table 1. For purposes of comparison, the same table also contains data for an accelerator-free mixture (rubber 100, sulfur 7, zinc oxide 5, and stearic acid 2 parts by weight).

TABLE 1

ACTIVATION ENERGY OF ADDITION OF SULFUR TO RUBBER

1	2	3	4	5
Accelerator	Kinetic constant of sulfur addition at 153° C	Activation energy of sulfur addition (cal. per mole)	Kinetic constant of constructive process at 153° C from Equation (1)	Activation energy of constructive process (cal. per mole)
Without accelerator	0.03	31,500	*	—
Tetramethylthiuram disulfide	0.33	22,900	0.4	21,900
Mercaptobenzothiazole	0.2	22,900	0.2	22,800
Diphenylguanidine	0.06	24,500	0.04	27,500

* As shown previously[1], Equation (1) does not apply to mixtures containing more than 3 per cent of sulfur; for this reason, calculation in the present case is impossible.

As was to be expected, accelerators appreciably increase the kinetic constants and reduce the activation energy of the process of addition of sulfur to rubber. The similarity between the values for this activation energy (Table 1, Column 3) and the analogous values (Column 5) calculated from Equation (1) for the constructive process demonstrates the correctness of the concept of the mechanism of vulcanization developed by the authors.

EFFECT OF ACCELERATORS ON INTERACTION OF RUBBER WITH OXYGEN

For the purpose of clarifying the effect of accelerators on the interaction of rubber with oxygen, special experiments on the oxidation of rubber in the presence of these substances were carried out.

The experiments were conducted in an adsorptiometer constructed in our laboratory by N. I. Nekrasov; this instrument made it possible to estimate the quantity of oxygen absorbed on the basis of the pressure change within the vessel containing the rubber. Different doses of accelerators were introduced into benzene solutions of the rubber. To prepare rubber films, the solutions were applied to glass, and the solvent was removed at room temperature. The rubber films had a thickness of 0.03 mm.; at this thickness, diffusion of oxygen

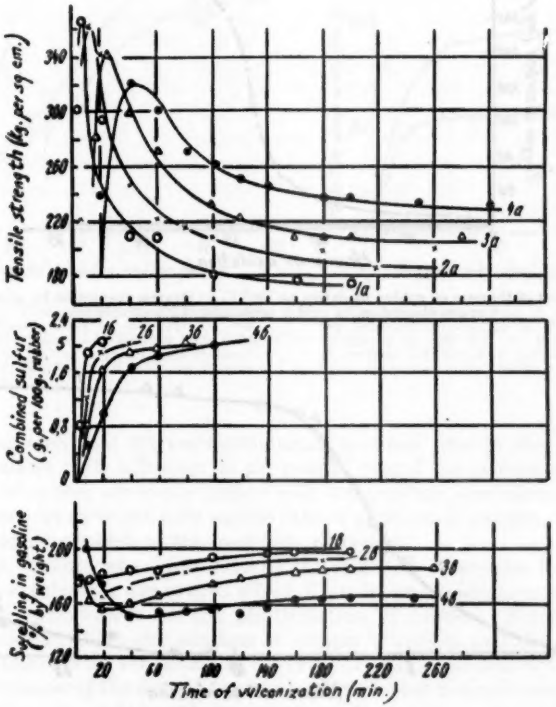

FIG. 8.—Vulcanization kinetics of thiuram-containing mixture at 123°, 133°, 143°, and 153° C (Curves 4, 3, 2, and 1). (a) Tensile strength; (b) Addition of sulfur to rubber; (c) Swelling in gasoline.

into the rubber does not control the oxidation process. In the present communication, only a few experiments are presented which characterize the general direction of the changes observed in the kinetics of the addition of oxygen to rubber in the presence of vulcanization accelerators.

The results, presented in Figures 9, 10, and 11, indicate that Captax accelerates the oxidation of rubber, while diphenylguanidine and thiuram retard this process. In addition, the experiments of Busse[5] on the plasticization of natural rubber in the presence of the same accelerators were repeated (Figure 12). Along with a confirmation of the acceleration of plasticization in the presence of Captax and diphenylguanidine (Figure 12, Curves 3 and 4), these data provide reasons for concluding that the above-mentioned accelerators increase the value of limiting plasticity. This effect is connected with the directive action of organic accelerators during the interaction of rubber with oxygen in the direction of intensified destruction of the rubber. This conclusion follows from the fact, established by the authors, that, in the presence of one and the same quantity of absorbed oxygen, the oxidation products of rubber obtained in the presence of Captax possess a lower viscosity (Figure 13).

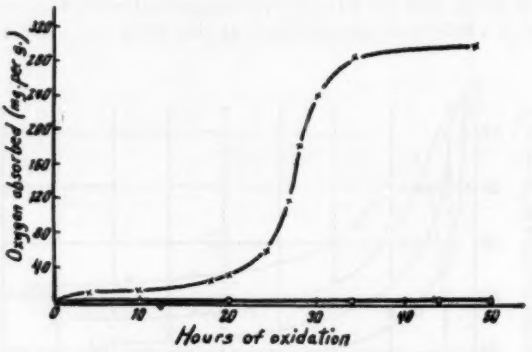

FIG. 9.—Effect of thiuram on rubber oxidation at 136° C. x: Oxygen absorption by pure rubber; o: Oxygen absorption by rubber containing 0.7% of thiuram.

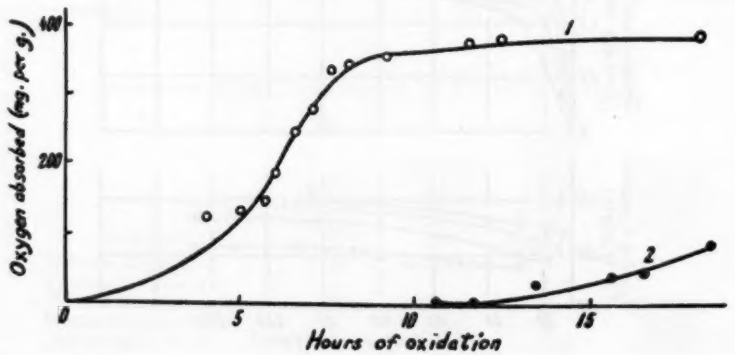

FIG. 10.—Effect of diphenylguanidine on rubber oxidation at 142° C. 1: Oxygen absorption by pure rubber; 2: Oxygen absorption by rubber containing 0.63% of diphenylguanidine.

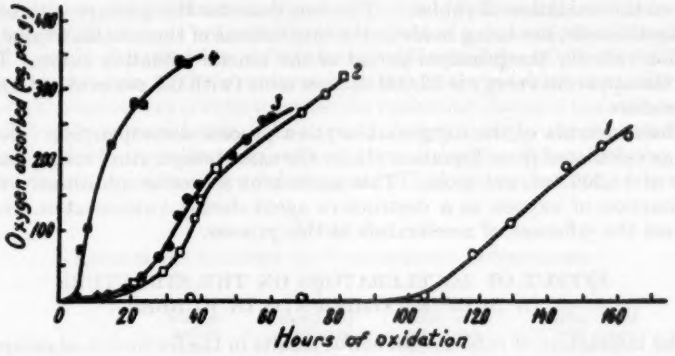

FIG. 11.—Effect of Captax on rubber oxidation at 100° and 120° C. 1: Oxygen absorption by pure rubber at 100° C; 2: Same at 120° C; 3: Oxygen absorption by rubber containing 0.78% of Captax at 100° C; 4: Same at 120° C.

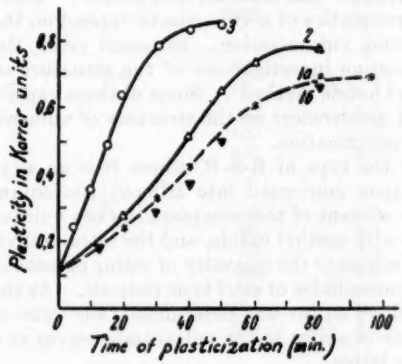

FIG. 12.—Kinetics of plasticization of rubber in closed mixer at 135–145° C. 1-a: Additive-free rubber; 1-b: Rubber with 0.8% of thiuram; 2: Rubber with 0.7% of diphenylguanidine; 3: Rubber with 0.6% of Captax. $a = 1$; $a = b$.

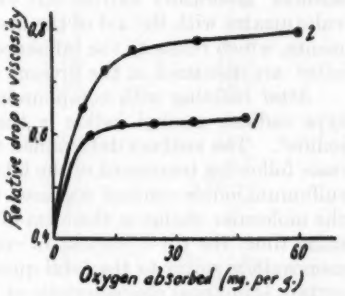

FIG. 13.—Relative drop in viscosity of rubber solutions as function of absorbed oxygen (oxidation at 120° C). 1: Relative viscosity of oxidized additive-free rubber solutions; 2: Same for rubber with 1.55% of Captax.

It is thus seen that tetramethylthiuram disulfide retards the addition of oxygen to rubber. Its influence on the overall rate of the process of oxidative destruction of rubber obviously differs with temperature conditions, inasmuch as this process depends not only on the rate of addition of oxygen, but also on the rate of decomposition of the oxidation products.

Although diphenylguanidine retards the addition of oxygen to rubber, it nevertheless accelerates the overall effect of oxidative destruction, as is apparent from the experiments on the plasticization of rubber. Mercaptobenzothiazole accelerates both the addition of oxygen to rubber and the decomposition of the latter under the action of oxygen. It was of undoubted interest to compare the values of the kinetic constants, as well as of the activation energies, of the processes connected with the addition of oxygen, as calculated, on the one hand, from Equation (1) and, on the other hand, from the direct kinetic

data on the oxidation of rubber. This was done for the mixture with mercaptobenzothiazole, use being made in the calculations of the constant value of the reaction rate for the principal period of the kinetic oxidation curve. In this case, the apparent energy is 12,000 cal. per mole (with 0.7 per cent of Captax in the mixture).

The constants of the oxygen-absorption process accompanying vulcanization, as calculated from Equation (1) for the same temperature range, lead to a value of 11,000 cal. per mole. This agreement serves as additional proof of the function of oxygen as a destructive agent during vulcanization and emphasizes the influence of accelerators in this process.

EFFECT OF ACCELERATORS ON THE STRUCTURE OF SULFUR COMPOUNDS IN RUBBER

The interaction of rubber with sulfur results in the formation of compounds possessing varying structures, depending on the number and location of the sulfur atoms. Weber[6] was one of the first to outline the possible structural types among the sulfur compounds present in rubber; recently, this subject attracted the attention of Brown and Hauser[7] and of Selker and Kemp[8]. There can be no doubt that the mechanical properties of a vulcanizate depend on the character of the structures formed during vulcanization. In recent years, the authors' laboratory carried out exhaustive investigations of the structure of vulcanizates with the aid of the methyl iodide method[9]. Some of these experiments, which relate to the influence of accelerators on the structure of vulcanizates, are discussed in the present communication.

After reacting with compounds of the type of R-S-R, where R is an allyl type radical, methyl iodide is thereupon converted into trimethylsulfonium iodide[8]. The authors determined the content of this compound in the vulcanizate following treatment of the latter with methyl iodide, and the tetramethylsulfonium iodide content was used to calculate the quantity of sulfur present in the molecular chains in the form of monosulfides of allyl type radicals. At the same time, the total content of combined sulfur was determined; the ratio of monosulfide sulfur to the total quantity of sulfur in the vulcanizate serves as a certain structural characteristic of the latter.

The investigation was carried out with vulcanizates the compositions of which are indicated in Table 2; the analytical results are presented in Table 3.

It is characteristic that vulcanizates of sodium-butadiene rubber without organic accelerators contain considerably less monosulfide sulfur combined with allyl type radicals than do similar vulcanizates of natural rubber. This may be explained in part by the existence in the latter of natural organic admixtures, which serve as vulcanization accelerators. As a matter of fact, supplementary

TABLE 2

COMPOSITION OF VULCANIZATES

Name of substance	Code designation of mixture					
	NK	NK-1	NK-2	SK	SK-1	SK-2
Smoked sheet	100	100	100	—	—	—
Sodium-butadiene rubber	—	—	—	100	100	100
Sulfur	7	7	7	7	7	7
Stearic acid	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5
Captax	—	0.3	—	—	0.3	—
Diphenylguanidine	—	—	0.378	—	—	0.378

experiments on the purification of natural rubber, followed by vulcanization, indicate a 20–30 per cent reduction in the content of monosulfides of the above-defined type in the resulting vulcanizates. Monosulfides of the R-S-R type constitute a fraction of the structures in vulcanizates in which the sulfur acts as a bridge, inasmuch as it links together the molecular chains of the rubber with the aid of main-valence forces. As a result of such linkage, a spatial structure is formed, which, in conformity with modern concepts, determines the most characteristic properties of the vulcanizate. Thus, vulcanization accelerators,

TABLE 3

RESULTS OF ANALYSES OF VULCANIZATES INVESTIGATED

1 Mixture code	2 Vulcanization time (minutes)	3 Total chemically combined sulfur (% of mixture)	4 Monosulfide sulfur with allyl type radicals (% of mixture)	5 Monosulfide sulfur (% of total chemically combined sulfur)
Natural rubber mixtures (NK)				
NK	200	4.9	0.35	7.1
	250	5.5	0.49	8.8
	300	5.9	0.53	8.8
				Av. 8.2
NK-1	20	3.8	0.29	7.6
	40	4.8	0.35	7.2
	60	5.4	0.49	9.1
	100	5.9	0.66	11.3
	300	6.1	0.83	13.7
				Av. 9.8
NK-2	10	1.0	0.09	10.0
	30	2.4	0.21	8.7
	40	3.0	0.31	10.2
	60	4.0	0.32	8.4
	90	4.8	0.47	9.9
	200	6.0	0.92	15.4
	300	6.1	0.95	15.6
				Av. 11.2
Sodium-butadiene rubber mixtures (SK)				
SK	20	1.4	0.04	2.9
	60	3.2	0.07	2.0
	80	3.8	0.09	2.4
	300	5.7	0.11	1.9
				Av. 2.3
SK-1	20	4.5	0.24	5.3
	40	5.4	0.28	5.2
	80	5.8	0.32	5.5
	150	6.0	0.37	6.1
	250	6.1	0.41	6.9
	300	6.1	0.44	7.1
				Av. 6.0
SK-2	10	0.7	0.05	6.6
	30	2.2	0.10	4.7
	40	2.6	0.14	5.3
	90	4.3	0.21	4.9
	200	5.7	0.37	6.5
	250	6.0	0.42	7.0
				Av. 5.8

by directing the process toward the formation of monosulfides, promote a more effective utilization of sulfur, in addition to aiding the formation of a structure which increases the mechanical strength of the vulcanizate.

INFLUENCE OF VULCANIZATION TEMPERATURE ON THE PARAMETERS OF KINETIC STRENGTH CURVE

The data of various authors[10] on the influence of temperature on the factors determining the optimum properties of vulcanizates fail to agree in many cases. Thus, according to some investigators, an increase in the vulcanization temperature results in lowering the tensile strength at the vulcanization optimum, whereas others have observed the opposite effect. Against the background of the early concepts of vulcanization as a homogeneous and unidirectional process, such data appeared to be contradictory. In the light of the concepts being developed by the present authors, vulcanization is a complex phenomenon, in which the properties of rubber change as a result of a combination of a series of simultaneous and in some cases oppositely directed processes. Acceptance of these views eliminates these apparent contradictions. As a matter of fact, if, during vulcanization, a mutual superimposition of two differently directed processes occurs, each of which possesses a separate positive temperature coefficient, the overall process may have either a positive or a negative temperature coefficient, depending on the correlation between the separate temperature coefficients and between the rates of the partial processes.

Good illustrations of these possibilities are provided by the cases of vulcanization in the presence of various accelerators discussed above.

As is seen from Figure 8, an increase in the temperature of vulcanization of the thiuram-containing mixture results in higher mechanical strength at the vulcanization optimum. This correlation becomes quite comprehensible when it is considered that thiuram greatly accelerates the interaction of rubber with sulfur and retards the interaction of rubber with oxygen. Thus, the relative temperature change in the rates of the two processes leads to an increase in the constructive effect. In mixtures containing Captax (Figure 7), an increase in temperature lowers the mechanical strength of the vulcanizate at the vulcanization optimum, indicating an intensification of the destructive processes as compared with the constructive process. Generally speaking, this result appears to be quite plausible, inasmuch as Captax accelerates the interaction of rubber with oxygen. A certain difficulty in the explanation proposed by the authors resides in the fact that, judging from the value of the energy of activation, the interaction with oxygen should have a lower temperature coefficient than the interaction with sulfur. In mixtures containing diphenylguanidine, the influence of temperature on the partial processes is more or less similar. As a result, the properties of the vulcanizate at the vulcanization optimum are practically independent of temperature. In all cases, the limiting strength of the vulcanizates decreases with rising temperature. As was indicated at the outset of the present communication, this parameter does not depend on the rates of the partial processes of interaction of rubber with sulfur and with oxygen, but is determined by the constants a' and b', which depend on the character of the molecular structure of the vulcanizate.

CONCLUSIONS

1. Vulcanization accelerators change all parameters of the kinetic strength curve during the vulcanization of natural-rubber mixtures with low sulfur contents.

2. Calculation of the kinetic constants of the fundamental vulcanization equation proposed by Dogadkin, Karmin, and Gol'berg shows that vulcanization accelerators affect both the kinetics of the interaction of rubber with sulfur and the kinetics of the interaction of rubber with oxygen.

3. Direct experiments on the oxidation of rubber have shown that tetramethylthiuram disulfide and diphenylguanidine retard the process of addition of oxygen to rubber, while mercaptobenzothiazole accelerates this process.

4. Data on the rate of plasticization and change in viscosity of rubber solutions during oxidation indicate that tetramethylthiuram disulfide and diphenylguanidine promote the disintegration of molecular chains of rubber during the oxidative destruction of the latter.

5. The activation energy of the process of oxidation of rubber in the presence of mercaptobenzothiazole corresponds to the activation energy calculated from the fundamental vulcanization reaction for the process of oxidative destruction. This provides additional proof of the participation of oxygen in the vulcanization process.

6. It has been established with the aid of the methyl iodide reaction that accelerators increase the bridge-sulfur content of the vulcanizate, which is present in the form of monosulfides, with one sulfur atom connected to an allyl type radical.

7. With increasing temperature, the tensile strength at the vulcanization optimum increases in mixtures containing tetramethylthiuram disulfide, decreases in mixtures containing mercaptobenzothiazole, and remains unchanged in mixtures containing diphenylguanidine. The limiting strength decreases in all cases with increasing temperature. This phenomenon is explained on the basis of the proposed concepts of the character of vulcanization kinetics and of the nature of the vulcanization optimum.

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THERMODYNAMICS OF CRYSTALLIZATION IN HIGH POLYMERS. VI. INCIPIENT CRYSTALLIZATION IN STRETCHED VULCANIZED RUBBER *

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From a consideration of the statistical thermodynamics of crystallization of rubber on stretching[1], it has been shown that the temperature (T_m) of incipient crystallization, *i.e.*, the highest temperature above which all crystallinity must disappear, should increase with the relative length α approximately in accordance with the relationship:

$$1/T_m^0 - 1/T_m = (R/h_f)\phi(\alpha) \tag{1}$$

where

$$\phi(\alpha) = (6/\pi n)^{\frac{1}{2}}\alpha - \alpha^2/2n - 1/\alpha n \tag{2}$$

Here T_m^0 is the crystallization temperature for the unstretched polymer ($\alpha = 1$), h_f is the heat of fusion per polymer segment, R is the gas constant, and n represents the number of statistical segments per chain between cross-linkages. With the object of establishing the dependence of T_m on α, we have measured the density of gum vulcanized rubber as a function of elongation at three temperatures, 20°, 40°, and 60° C, abrupt increase in density being used as the criterion for the onset of crystallization[2]. Experimental difficulties are formidable, and they were not entirely overcome in the work reported here. Inasmuch as it has been necessary to abandon further work on this project, the significant results which have been obtained are set forth briefly below.

EXPERIMENTAL

Each of six molded rubber bands[3], 0.1 × 1.0 cm. in section and having a circumference of 10 cm., was marked at distances $L_0 = 3.00$ cm. apart on its outer surface. The bands were evenly stretched about pairs of aluminum support rods $\frac{3}{16}$ inch in diameter, which were inserted through appropriately spaced holes drilled (perpendicular to the axis) through an aluminum tube 20 inches long and ½ inch in diameter. The holes were so arranged as to provide relative lengths α from 1.0 to 10 in steps of 0.25. This assembly, suspended by a thin wire from one arm of an analytical balance, was immersed in water contained in a tall glass cylinder located in a water thermostat regulated to ±0.01° C. Weighings were accurate to the nearest milligram.

In carrying out an experiment, the unstretched bands were weighed in air and then in water at the temperature of the experiment. After stretching at room temperature to the desired elongation, they were held in water at a high

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temperature (either 70° or 90°) for ten minutes to melt crystallites which may have been formed. The bands were quickly transferred to the constant temperature bath and the weight was determined after thirty minutes. On removal from the bath, the distances between the marks were measured first in the stretched condition (L_s) and then unstretched (L_0''). They were again stretched at room temperature and the cycle repeated.

RESULTS

The distance L_0'' between the marks on the bands on release of tension assumed successively larger values as the measurements proceeded from one elongation to the next, etc. This residual elongation was reduced slightly by immersion of the bands in petroleum ether (and drying in vacuo) and hence was due in part to slow elastic recovery. The remaining permanent set has been attributed[4] to a reversible breaking and reforming of chemical bonds between chains while the rubber is under tension. On release of tension, the bonds which were formed while the sample was stretched oppose contraction of the rubber[5]. The resulting increase in L_0 appears to be characteristic of the modified network structure and must, therefore, be accounted for in the calculation of the elongation. As an approximate corrective measure, α has been taken equal to L_s/L_0', where L_0' represents the distance between the marks after removal of the load and relaxation by solvent treatment. In practice L_0' was obtained from the observed values of L_0'' by means of a calibration curve relating the two lengths.

Density-time studies made 40° indicated that, although the major portion of the density change had occurred within thirty minutes, the time necessary to attain an apparent equilibrium varied from at least one hour at low elongation

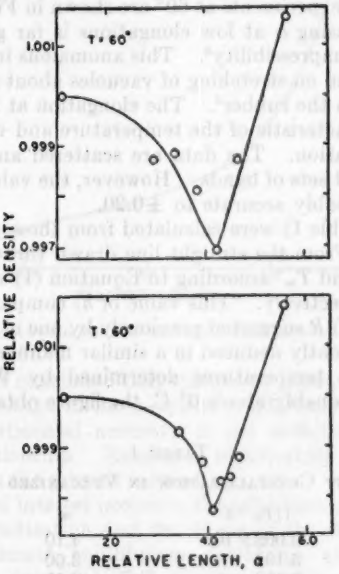

FIG. 1.—Density-elongation curves obtained at 60° for two similar sets of bands.

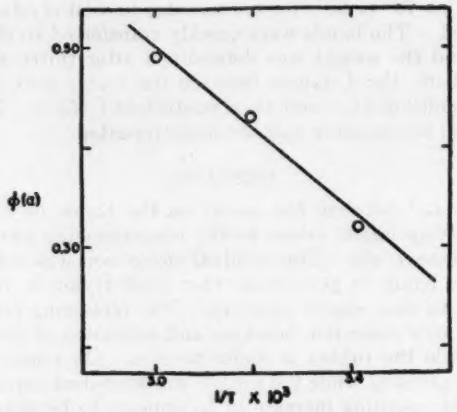

FIG. 2.—The relation between the incipient crystallization temperature and the elongation, plotted at $1/T_m$ (°A^{-1}) *vs.* $\phi(\alpha)$.

to at least ten hours at elongations above the crystallization point. In view of the occurrence of stress relaxation, such prolongation of the experiments obviously was impractical. While the equilibrium curve probably would differ from that reported here, the equilibrium elongation at which the density suddenly increases doubtless would occur near the position observed in these experiments. Hence, we believe that the present method yields a useful approximation to the equilibrium point for incipient crystallization.

The results of two experiments at 60° are shown in Figure 1. The decrease in density with increasing α at low elongations is far greater than would be calculated from the compressibility[6]. This anomalous increase in volume may be due to the formation on stretching of vacuoles about solid vulcanization ingredients embedded in the rubber[7]. The elongation at the minimum point of the curve (α_c) is characteristic of the temperature and was taken as the point of incipient crystallization. The data are scattered and are not entirely reproducible for different sets of bands. However, the values of α_c at 20, 40, and 60° (Table I) are probably accurate to ± 0.20.

Values of $\phi(\alpha)$ (Table I) were calculated from these data by Equation (2), assuming $n = 100$. From the straight line drawn through the plot in Figure 2 of $1/T_m$ *vs.* $\phi(\alpha)$, h_f and $T_m°$ according to Equation (1) were found to be 400 R cal. and $-17°$ C, respectively. This value of h_f compares favorably with the estimate of 600 (± 300) R suggested previously by one of the authors[1], and with the value of 465 R recently deduced in a similar manner by Goppel[8], using incipient crystallization temperatures determined by Wildschut. While the true value of $T_m°$ is probably above 0° C, the figure obtained here is similar to

TABLE 1

INCIPIENT CRYSTALLIZATION IN VULCANIZED RUBBER

T_m	$1/T_m$, °A^{-1}	α_c	$\phi(\alpha)$
60°	3.003×10^{-3}	4.10	0.48
40	3.195	3.60	0.43
20	3.413	2.50	0.31
		1	0.12

that (−20 °C) employed by Goppel. The discrepancy may be due in part at least to the admitted failure of the theory at low elongations[1].

The choice of n above is somewhat arbitrary. Fortunately the values of h_f and $1/T_m^0$ are rather insensitive to the choice of n. The equilibrium force of retraction at 100 per cent elongation, 78 lbs. per sq. in., is comparable to that obtained for a rubber vulcanizate known to contain on the average of 100 isoprene units between cross-linkages[9]. Hence, we conclude that the chains in this particular vulcanizate are about 100 units long. The configurational segment is not necessarily identical with the structural unit, however.

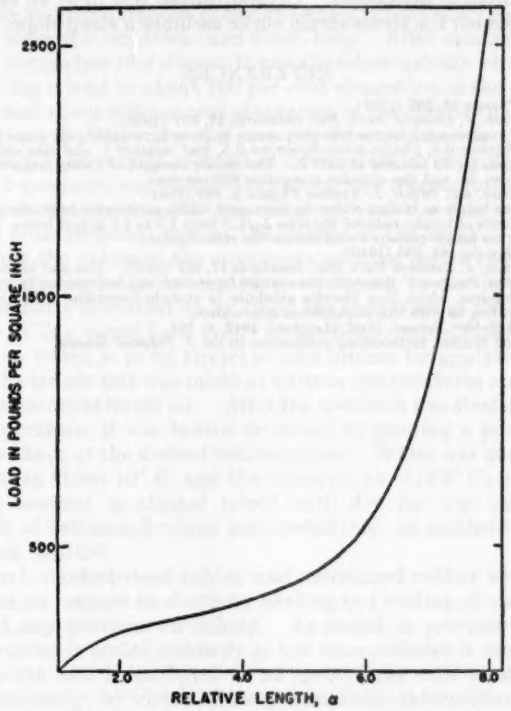

FIG. 3.—The stress-strain curve for the rubber bands at room temperature.

From these data it is concluded that the theory predicts correctly the order of magnitude for the change in the incipient crystallization temperature with elongation. The experimental accuracy is not sufficient to determine the exact form of the relationship. Results of significantly greater accuracy are not to be expected from the present method.

A point of additional interest occurs in the relationship between the elongation for incipient crystallization and the shape of the stress-strain curve. Although under approximate equilibrium conditions at room temperature incipient crystallization occurs at $\alpha \cong 3$, the stress-strain curve (Figure 3) does not exhibit a sharp break until a relative length α of at least 5 has been reached.

Obviously the break in this curve must not be identified with the elongation necessary for incipient crystallization. The break in the curve presumably represents the region in which the degree of crystallinity becomes large.

SUMMARY

Experimental determination of the elongation at which crystallization commences in vulcanized rubber has been attempted through measurement of density changes by a hydrostatic method. The critical elongation for incipient crystallization appears to depend on the temperature, in approximate accordance with theoretical prediction. Crystallization sets in at an elongation well below that at which the stress-strain curve assumes a steep slope.

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[2] Holt and McPherson, *J. Research Nat'l. Bur. Standards* **17**, 657 (1936).
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[4] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **5**, 380 (1944).
[5] Immersion of these bands in boiling water (a treatment which accelerates both viscous relaxation and chemical rupture of bonds) reduced the ratio L_2/L_0'' from 1.3 to 1.1 in four hours, with an indication that heating for longer periods would reduce the ratio further.
[6] Gee, *Trans. Faraday Soc.* **42**, 585 (1946).
[7] Holt and McPherson, *J. Research Nat'l. Bur. Standards* **17**, 657 (1936). Gee and his collaborators of the British Rubber Producers' Research Association have observed independently a similar anomalous increase in volume, which they likewise attribute to vacuole formation. We are indebted to Dr. Gee for providing us with this unpublished information.
[8] Goppel, *Proc. 2nd Rubber Technol. Conf.* (London), 1948, p. 164.
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THE TENSILE STRENGTH OF RUBBER AND RUBBER MOLECULE *

CHULLCHAI PARK AND USABURO YOSHIDA

The writers prepared ribbons of smoked-sheet rubber and vulcanized rubber, each 0.5 cm. wide, 0.3 cm. thick, and 6 cm. long. After marking two points 1 cm. apart on the surface of a ribbon, it was stretched quickly at room temperature by applying a load to about 700 per cent elongation in the case of smoked sheet rubber and about 400 per cent elongation in the case of vulcanized rubber. At these degrees of elongation, the samples were assumed to be considerably crystallized and to be mostly relieved of intermolecular slipping by stretching. The stretched specimen was then broken at various temperatures by increasing the load, and its tensile strength was obtained from the value of the breaking load and the cross-sectional area at the instant of the break. The latter was calculated from the values of the cross-sectional area before stretching and the changes of length and density caused in stretching to the final break. The actual experiment was carried on by using the apparatus as shown in Figure 1. In this figure, V is a vessel fixed firmly to the heavy table T, and S is the test-piece of rubber which is to be stretched and broken by applying load W over pulley P. The tensile test was made at various temperatures ranging from 78° C to the temperature of liquid air. After the specimen was stretched sufficiently at room temperature, it was heated or cooled by pouring a proper liquid or a liquid mixture kept at the desired temperatures. Water was used for temperatures higher than about 10° C, and the liquid air at −185° C; for intermediate temperatures acetone or alcohol mixed with dry ice was employed. Two different kinds of vulcanized rubber were tested: *viz.*, an accelerator mixture and a carbon black mixture.

As a control, smoked-sheet rubber and vulcanized rubber were broken suddenly in the same manner as above by heating and cooling at various temperatures without any previous stretching. As stated in previous papers[1], when unstretched rubber is cooled suddenly at low temperatures it undergoes almost no crystallization and is hardened as an amorphous solid in the supercooled state. Consequently, by virtue of the predominant intermolecular slipping, a very low value of the tensile strength was expected when compared with the specimen cooled in the stretched state. The results obtained are shown in Figure 2, by plotting the temperature as abscissa and the tensile strength as ordinate. In this figure the curves in solid lines refer to the specimens broken by being cooled or heated in the stretched state; those in broken lines refer to the specimens broken by being cooled or heated suddenly when unstretched; and the dots, crosses, and small circles represent, respectively, the tensile strengths of smoked-sheet rubber, vulcanized rubber of the accelerator mixture B, and vulcanized rubber of the carbon black mixture C. As seen in the figure, the tensile strengths of the smoked sheet rubber and vulcanized rubber which were cooled or heated while stretched increase generally with decrease in tem-

* Reprinted from the *Memoirs of the College of Science*, Kyoto Imperial University, Series A, Vol. 24, No. 2, pages 109–116, March 1944.

perature. They are generally very different from each other, being considerably higher for the vulcanized rubber C, but they converge to almost the same value at the temperature of liquid air. This point is especially noteworthy, as will be described later. As to the smoked sheet rubber and the vulcanized rubber B, which were broken by being cooled suddenly while unstretched, their tensile strengths were entirely different from those of the specimens kept stretched at low temperatures. As would be expected, the tensile strengths decreased in this case, in contrast to the stretched specimens, with decrease of the temperature from about $-20°$ to about $-70°$ C, and then increased slightly at the temperature of liquid air.

As to the ultimate mechanism of the breaking of the rubber ribbon by stretching, two phenomena are conceivable: (1) mutual slipping between neighboring chain molecules, and (2) tearing of the chain molecules themselves at the weakest points in their chain structure. When a ribbon of smoked-sheet rubber is stretched very slowly at room temperature, it becomes gradually

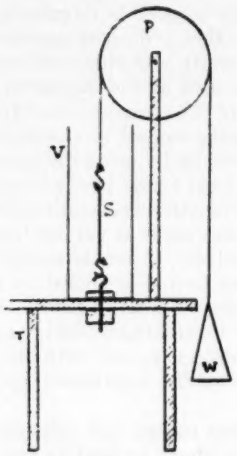

FIG. 1.

thinner at some portion, without being crystallized noticeably, and then undergoes final rupture. As the elongation of the broken pieces does not recover much on heating, rupture of the rubber ribbon in this case seems to be mainly caused by the intermolecular slipping. However, in the present experiment, the rubber ribbons were broken by suddenly increasing the stretching load by cooling in a strongly stretched or entirely unstretched state, and rupture took place with a right section as if the ribbon had been cut with a sharp knife, without becoming gradually thinner as described above. Thus, in rupture in this case, tearing of the long chain molecules presumably takes place together with intermolecular slipping, though the proportionate weight of these two factors differs according to the conditions to which the test-pieces are subjected.

Whether or not rupture of the rubber ribbon in any particular case is due chiefly to tearing of long chain molecules will be judged by knowing under what conditions the intermolecular slipping takes place with difficulty. Figure 3, which has been shown in a previous paper[2], represents the permanent elongation

of the smoked-sheet rubber ribbons caused by intermolecular slipping when the ribbons are kept stretched for different times at room temperature. As is seen from the figure, intermolecular slipping decreases generally as the degree of crystallization increases with sufficient stretching. With extreme stretching (to greater than about 5.5 times the original length), no trace of intermolecular slipping can be detected, even when the specimen is kept for 37 days in the stretched state at room temperature, except a small permanent elongation caused by the initial sudden stretching. On the contrary, when crystallization is not predominant because of insufficient stretching, noticeable intermolecular slipping, which is roughly proportional to the stretching stress and the amount of uncrystallized part, proceeds gradually during the time the specimen is kept stretched. Further, it has been reported in the previous paper that intermolecular slipping is considerable at high temperatures and decreases with

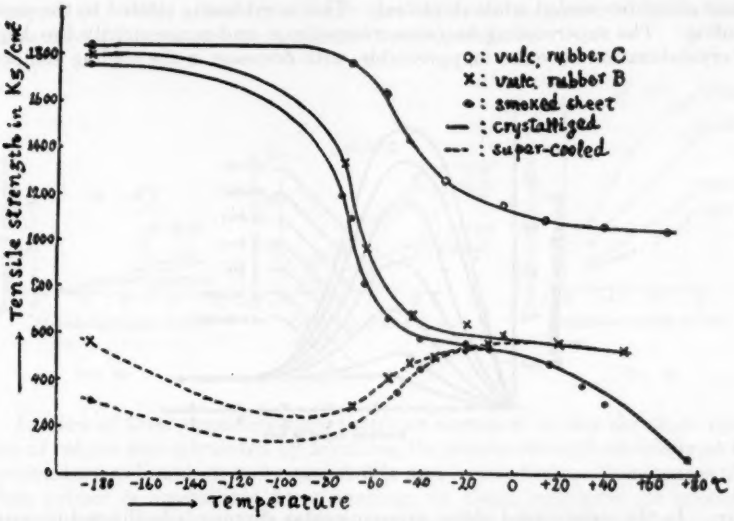

FIG. 2.

lowering of the temperature. Consequently it may be inferred from these facts that, when a highly stretched rubber ribbon is cooled to the temperature of dry ice or of liquid air, intermolecular slipping becomes very difficult, and tearing of the long-chain molecules of rubber at the localities of the weakest interatomic cohesion becomes the main cause of rupture by stretching of the specimen.

Measurements were made of the permanent elongations of vulcanized rubber ribbons of the carbon black mixture caused by intermolecular slipping in a stretched state. The rubber ribbons were kept stretched for various times in three different temperature ranges, *viz.*, 12°–18° C, 30°–40° C, and 50°–60° C. The permanent elongations of the specimens were obtained as before by putting the specimens in boiling water for a short time after release so that they could completely contract, and then measuring the elongation per original unit length. The results are shown in Figures 4a, 4b, and 4c. If we compare these figures

with Figure 3, we find that the permanent elongation due to intermolecular slipping is very much smaller for vulcanized rubber than for unvulcanized smoked sheet. Though the permanent elongation is considerable at 30°–40° C or 50°–60° C, it is almost inappreciable at room temperature (12°–18° C), even with stretching for 31 days; and there is hardly any difference between stretching of 31 days and for only a second. This is one of the valuable properties of vulcanized rubber, and it seems to be caused by the hindrance of intermolecular slipping by virtue of the strong side linkage between neighboring chain molecules of the rubber, due to the presence of the sulfur molecules.

When unstretched rubber is cooled suddenly to such a low temperature as −30° C, crystallization is suspended, and the rubber hardens to an amorphous solid by being supercooled as stated above. It has also been pointed out that the tensile strengths of smoked-sheet rubber and vulcanized rubber which are cooled suddenly while unstretched are remarkably low when compared with those of rubber cooled while stretched. This is evidently related to the supercooling. The supercooling becomes conspicuous, and consequently the degree of crystallization becomes inappreciable, with decrease in the cooling tempera-

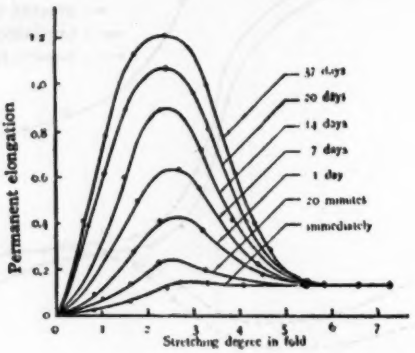

FIG. 3.

ture. In the supercooled state, intermolecular slipping is facilitated by virtue of the lack of some kind of linking effect between neighboring molecules, which is remarkable in the crystallized state. The fact that the tensile strength of rubber ribbons which are cooled suddenly while unstretched decreases from −20° to about −70° C is thus clearly understood by the increase in the degree of the supercooling with lowering of the temperature. When the cooling temperature is lowered still more to that of liquid air, the tensile strength increases slightly. By sudden cooling to this low temperature, supercooling is almost perfect, and a slight increase in tensile strength at this temperature seems to be caused by the increased difficulty of intermolecular slipping, due to the increased side cohesive force between neighboring chain molecules.

The tensile strengths of vulcanized rubber and smoked-sheet rubber which are kept cooled in the fully stretched state increase with decrease of the cooling temperature, that of the vulcanized rubber C being generally much higher than those of the other kinds. This superior tensile strength of the vulcanized rubber C can be explained by the interfering action of sulfur molecules on intermolecular slipping by virtue of the enhanced side linkage between neighboring

chain molecules; and the increase of the tensile strengths of the vulcanized rubber and the smoked-sheet rubber with decrease of temperature can be ascribed to the increased difficulty of intermolecular slipping as a result of the increased degree of crystallization and of intermolecular side cohesion at low temperatures. The tensile strengths of vulcanized rubber C and the other kinds, which are considerably different at higher temperatures, converge almost to the same value at the temperature of liquid air. This point is especially noteworthy, and it seems to indicate that the tensile strengths of all vulcanized and smoked-sheet rubbers at this low temperature are mainly related to the force which is necessary to tear the chain molecules of rubber; for, if they were still due to a considerable extent to intermolecular slipping, the remarkable differences at higher temperatures should also be present at the temperature of liquid air. Further, as is seen in Figure 2, at the temperature of dry ice, the tensile strength of vulcanized rubber C reaches almost its maximum value for the temperature of liquid air. This seems to indicate that the force necessary to tear a chain molecule of rubber is not much affected by temperature.

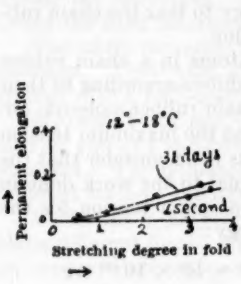

FIG. 4a

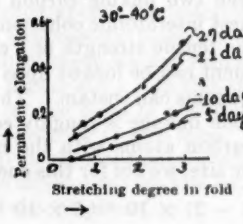

FIG. 4b

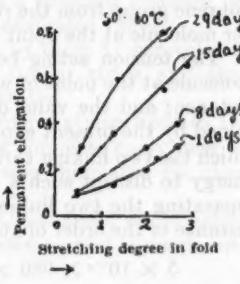

FIG. 4c

In view of these considerations, the force necessary to tear the chain molecule of rubber was calculated by assuming the tensile strength of rubber at the temperature of liquid air to be exclusively due to this force. It is known that when rubber is crystallized by stretching, its chain molecules are arranged parallel to the direction of stretching, and that four such chain molecules pass through its unit crystal having the cross-sectional area of $8.54 \times 12.64 = 108$ A^2 in the direction perpendicular to that of stretching. Thus if we assume that all rubber molecules in a rubber ribbon which is fully stretched and cooled to the temperature of liquid air are approximately fitted in the crystal lattice, the total number of chain molecules penetrating the cross-sectional area of 1 sq. cm. is $(4/1.08) \times 10^{14} = 3.7 \times 10^{14}$. Moreover, if we take the tensile strength of the fully stretched rubber ribbon at the temperature of liquid air as 1850 kg. per sq. cm., the force necessary to tear a chain rubber molecule becomes $(1.85 \times 10^6)/(3.7 \times 10^{14}) = 5 \times 10^{-9}$ g., which may be called the *tensile strength of the chain rubber molecule.*

It is known that the decomposition of rubber into isoprene (C_5H_8), dipentene ($C_{10}H_{16}$), and heveene (constitution unknown) begins at about 200° C; and this fact makes it possible to make a rough estimate of the energy necessary to decompose one isoprene group. The character of thermal motion of each part of the long chain molecule is of course not obvious, but if the mean kinetic energy of an isoprene group is taken as the same as that of a gas molecule at

the same temperature, then the simple kinetic theory of gases can be applied. If we represent by m and $\overline{V}^2$ the mass and the mean square velocity of a gas molecule, then the average kinetic energy of a molecule at an absolute temperature T is given by:

$$\frac{1}{2}m\overline{V}^2 = \frac{3}{2}\frac{R}{N}T$$

where R is the gas constant ($R = 1.985$ cal. per degree) and N is the Loschmidt number ($N = 6 \times 10^{23}$). If we take T as $200° + 273°$ K, at which the decomposition of rubber molecules into isoprene and others takes place, we get the value of:

$$\frac{1}{2}m\overline{V}^2 = 9.8 \times 10^{-14} \text{ erg}$$

as the mean kinetic energy of a gas molecule. If this value is taken to be the same as the mean kinetic energy of an isoprene group as a whole at the same temperature, it can be considered to be roughly the energy to decompose one isoprene group from the rubber molecule, *i.e.*, the energy to tear the chain rubber molecule at the point of weakest interatomic cohesion.

The tension acting between two linking carbon atoms in a chain rubber molecule at the point of weakest interatomic cohesion differs according to their distance; and the value of the tensile strength of a chain rubber molecule obtained by the present experiment can be looked upon as the maximum tension which the two linking carbon atoms can sustain. Thus if we consider that the energy to disrupt such a carbon linkage is roughly equal to the work done in separating the two linking carbon atoms with the maximum tension for the distance of the order of atomic size, we get for this energy:

$$5 \times 10^{-9} \times 980 \times (1 \sim 2) \times 10^{-8} \fallingdotseq 5 \times 10^{-14} \sim 10 \times 10^{-14} \text{ erg}$$

which is in good accord with the former estimation.

The above way of estimating the energy required to break the weakest carbon linkage in the chain rubber molecule is very rough, of course. However, the agreement between the values estimated in two different ways is satisfactory; and it may be looked upon as confirming the value obtained by the present experiment as of the right order for the tensile strength of the chain rubber molecule. The tensile strength of the chain rubber molecule is related to the point of the weakest interatomic cohesion in it; and it is natural to designate the part linked by a single bond between carbon atoms as such as the weakest interatomic cohesion.

SUMMARY

The tensile strengths of crystallized crude rubber and vulcanized rubber are remarkably different from each other at room temperature, but are found to be almost the same at the temperature of liquid air. By assuming that the tensile strength of crystallized rubber at this low temperature is entirely due to its chain molecules, the forced needed to break a chain molecule of rubber at its weakest point is estimated.

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FREE RETRACTION OF ELONGATED RUBBERS *

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THE RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

Measurements of the speed of retraction have been reported recently by Stambaugh, Rohner, and Gehman[1], by Mrowca, Dart, and Guth[2], and by Wildschut[3].

The first authors investigated the speed of retraction by means of a photoelectric unit which records the time necessary for the end of a strained strip of rubber to pass between two fixed points. The measured time depends on the position of the fixed points, as the speed of the end of the strip is not constant during the retraction. Generally these authors kept a constant distance between the fixed measuring points and one end of the elongated rubber.

The whole movement of the tip was characterized by them by one velocity constant. They also photographed the retracting rubber strips and steel springs with a high-speed stroboscopic Edgerton apparatus.

Mrowca, Dart, and Guth[2] made similar studies with a stylus fixed to the moving end of a strained rubber strip. In this case a complete curve may be obtained. The influence of the mass of the stylus was eliminated by using different styluses and extrapolating to zero mass.

Wildschut in his recent book[3] mentioned studies about speed of retraction along different lines. The subsequent studies have been carried through with an improved apparatus of the latter author.

EXPERIMENTAL

The principle of the measurement is shown in Figures 1a and b.

A small rubber ring is stretched between points A and B and can be set free at one end by means of a tumbler device at B. The rubber ring springs back to point C. The force necessary for the elongation is measured by the weight W. The distances AB and AC can be adjusted to different initial and final elongations, respectively. As soon as the end of the rubber ring leaves B, contact K_1 is opened and, on arriving at C, the rubber ring opens a second contact K_2. Between the opening of the two contacts the condenser Cd discharges through the resistance R, and the drop in potential is read on an electrostatic voltmeter V. The drop in potential is a measure of time defined by:

$$V_t = V_0 e^{-\frac{t}{RC}} \qquad t = RC \ln \frac{V_0}{V_t}$$

where V_t = potential at time t
V_0 = potential at time o
R = resistance in ohms
C = capacity of condenser in farads

In every set of measurements the initial elongation, defined by AB, was kept constant at, for instance, 450 per cent, whereas the final elongation of the jump was lowered stepwise to 425, 400 percent, etc., by displacing C.

* Reprinted from the *Proceedings of the Second Rubber Technology Conference* (London), June 23–25, 1948, pages 190–203.

Before every set of measurements, the strained rubber was allowed to relax for at least 1 hour so as to make sure of constant stress during the whole series of measurements. This turned out to be necessary, since the repeated elongating and retracting causes a quick decrease of stress in unrelaxed rubber. The constancy of the stress was controlled by balancing the force against the weight W. In those cases where the stress showed a decrease during the measurement, the results were discarded.

The rings were punched from cured sheets about 1 mm. thick of a rubber compounded as shown in Table I.

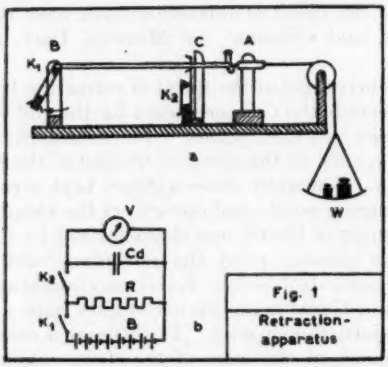


FIG 1.

For the unstretched length L_0 of the rings, half the average circumference minus half the circumference of one pulley plus the diameter of one pulley was taken.

Results were calculated to an unstretched length of 10 cm., assuming a direct proportionality between time and unstretched lengths.

RESULTS

Graphs were obtained in which elongation $\lambda\left(=\frac{L-L_0}{L_0}\right)$ was plotted against time for natural rubber, Buna-S, Perbunan, Neoprene-GN, Neoprene-FR, Hycar OR-15 and OR-25, Butaprene-NXM and Butyl rubber. These graphs[4] are shown in Figures 2 to 7, and 9 to 12.

For pure-gum vulcanizates of synthetic rubbers (except Neoprene) no measurements could be made from initial elongations higher than about 200 per cent. These rubbers at higher elongations do not pass the periods necessary for relaxation to constant stress.

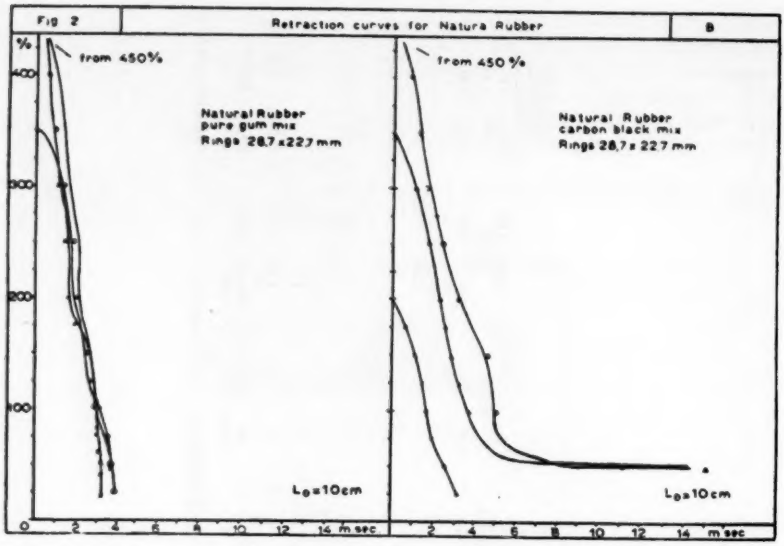
DISCUSSION OF THE RESULTS

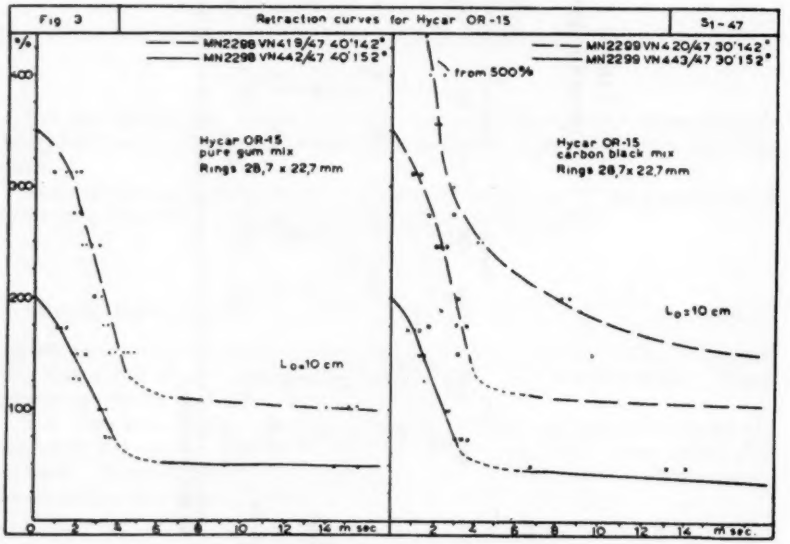
The authors already mentioned measured principally the velocity of the tip of an elongated and released rubber strip in space, whereas these studies are concerned with the movement of the loose tip of the retracting rubber relative to the other end. Both velocities are identical as long as the fixed end is motionless. Classical theory requires that, after complete retraction, the whole of the rubber be in motion with the same velocity as the loose tip.[5]

TABLE 1
COMPOUNDS USED

	NW		Buna-S		Perbunan		Neoprene		Butyl		Hycar OR 15/25		Polymethylpentadiene Homopol*	Polymethylpentadiene Copol
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	10	10	12	5	15	5	5	3	3	5	5	5	5
Antioxidant	1.5	1.5	1	1	1	2	2	2	—	—	—	—	—	—
Altax	—	—	—	—	—	—	—	—	—	—	1.25	1.25	—	—
Captax	0.8	0.8	—	—	—	—	—	—	0.5	0.5	—	—	1.5	1.5
D.P.G.	0.5	0.5	—	—	—	—	—	—	—	—	—	—	—	0.2
Vulc. AZ	—	—	1.8	1.8	1.8	1.8	—	—	—	—	—	—	—	—
Tuads	—	—	—	—	—	—	—	—	1.0	1.0	—	—	0.4	—
Carbon black	—	44	—	52	—	57	—	30	—	50	—	50	(50)	(50)
Dibutyl phthalate	—	—	—	—	—	—	—	—	—	—	—	20	—	—
Tricresyl phosphate	—	—	—	18	—	30	—	—	—	—	—	—	—	—
Stearin	1	2	2	2	2	2	0.5	0.5	1	1	1.5	1.5	—	—
Other softeners	—	10	—	10	—	10	—	—	—	—	—	—	5	5
Sulfur	1.75	2	1.5	1.5	1.5	1.5	—	—	2	2	1.25	1.5	2.5	2.5
Extra light magnesia	—	—	—	—	—	—	4	4	—	—	—	—	—	—
Vulcanization	20 mins.	142° C	20 mins.	142° C	25 mins.	142° C	15 mins.	153° C	40 mins.	153° C	30–45 mins.	153° C	30–80 mins.	145° C

* The homopolymer consists of 85 per cent 2-methyl-1,3-pentadiene and 15 per cent of 2-methyl-2,4-pentadiene. In the copolymer, 80 per cent of this mixture is copolymerized with 20 per cent of butadiene.

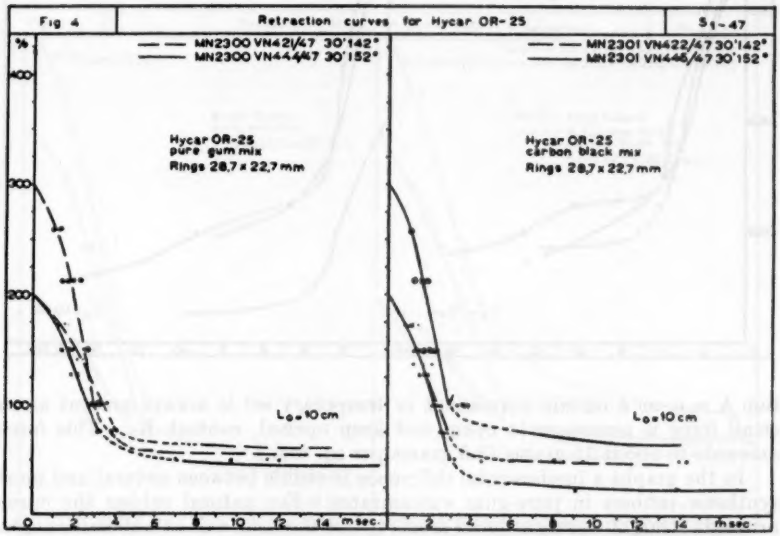


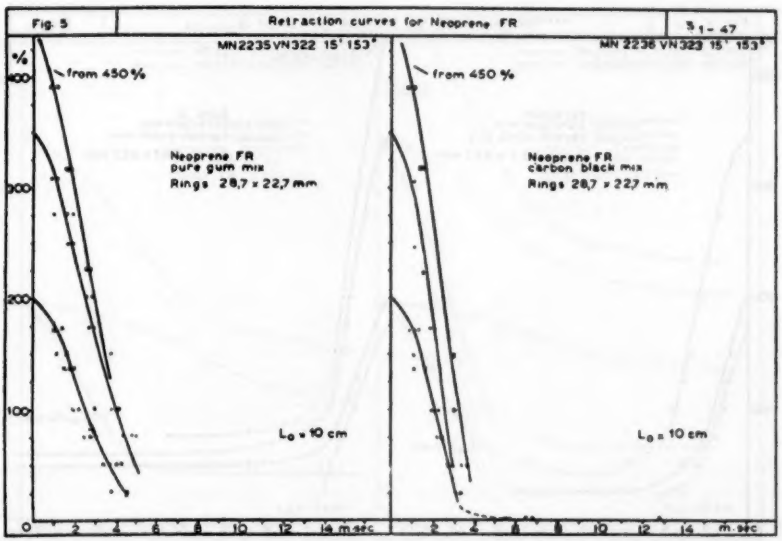


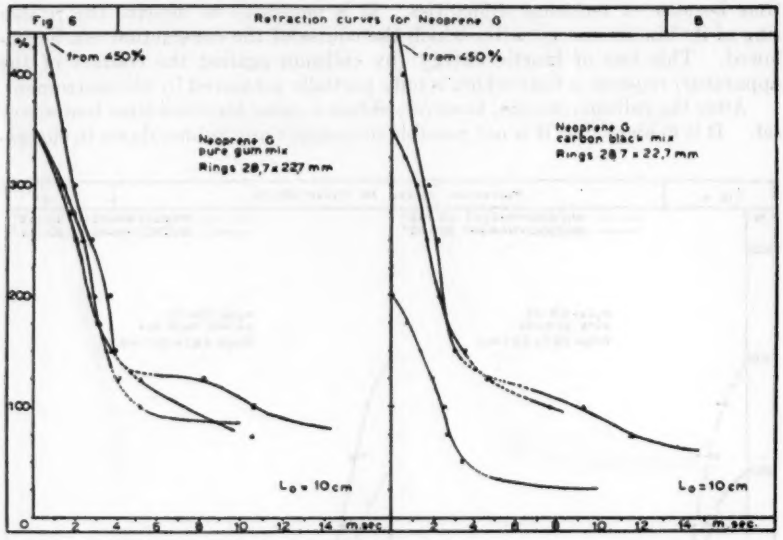
If the rubber were not held at the fixed end, the whole piece after complete retraction would fly through space with undiminished velocity except for the friction of the air. During this time, however, the distance between the ends of the strip is not necessarily constant. The strip continues to contract (elastic after-effect), though it never again reaches its original length. The course of this after-contraction cannot yet, however, be followed exactly in

time because of technical difficulties. It is necessary to deprive the rubber ring of its kinetic energy, after which the course of the contraction can be followed. This loss of kinetic energy (by collision against the contact of the apparatus) requires a time which is only partially measured by the instrument.

After the collision we can, however, obtain a value for short-time temporary set. It is evident that it is not possible to measure any rubber down to elonga-

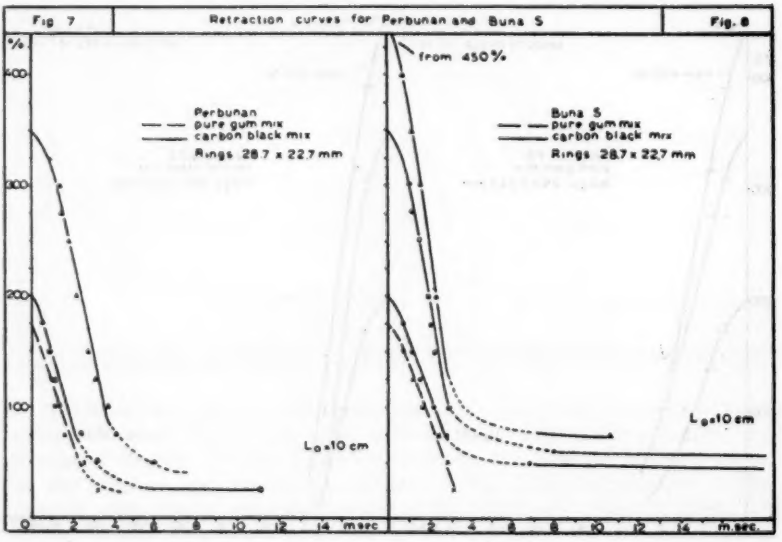






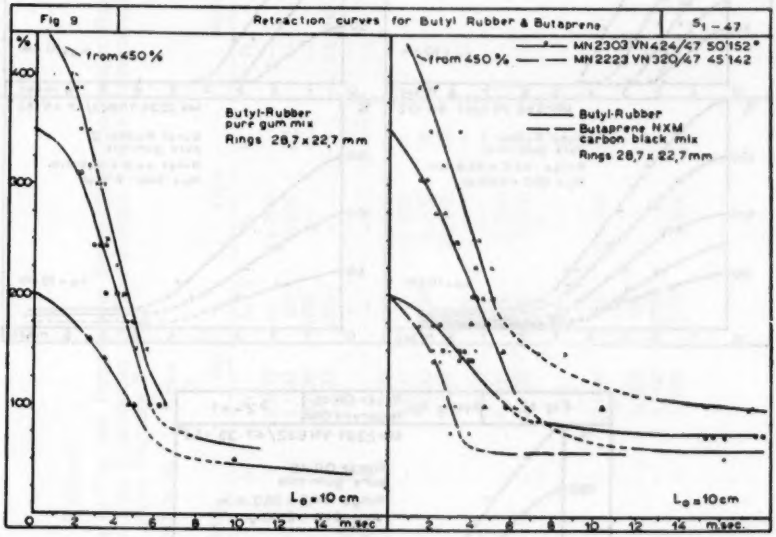
tion $\lambda = o$, as a certain permanent or temporary set is always present and a small force is necessary to open, and keep opened, contact K_2. This force amounts to about 15 grams (2.5 grams per sq. mm.).

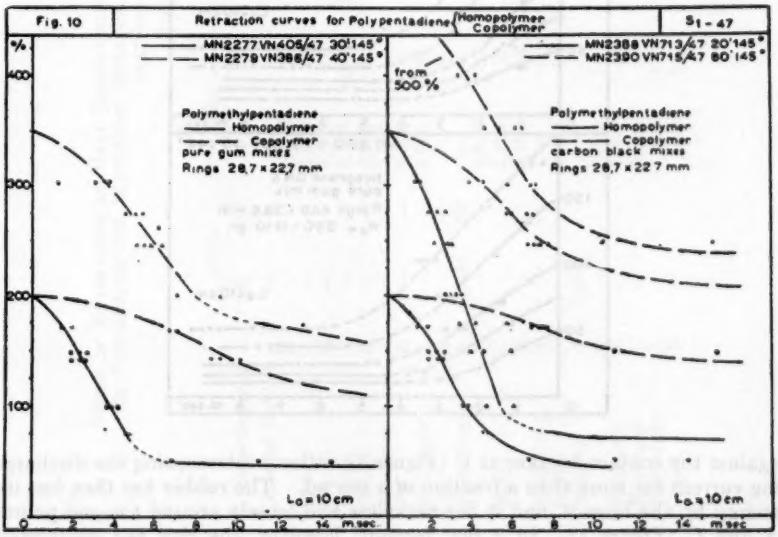
In the graphs a fundamental difference is visible between natural and most synthetic rubbers in pure-gum vulcanizates. For natural rubber the curve proceeds straight downward and seems to cut the time axis at a definite angle.



For synthetic rubbers, the slope of the curve decreases in the second part of the retraction and finally seems to approach asymptotically to a constant value for much longer times. This is due to permanent (or temporary) set and is found also for natural rubber at higher elongation, especially in the carbon black mix.

What really happens can be observed when choosing a low final elongation with a synthetic rubber such as Hycar-OR. The retracting rubber collides





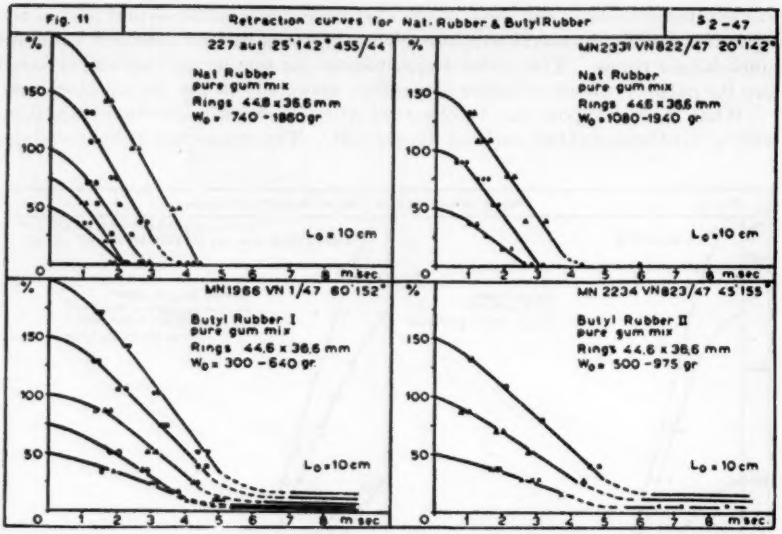
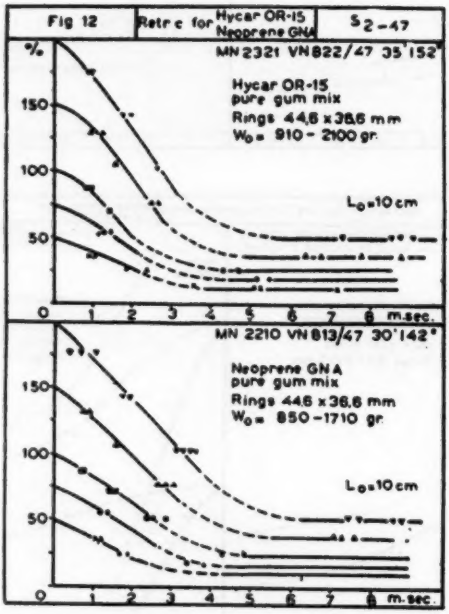


Fig. 11
Retraction curves for Nat-Rubber & Butyl Rubber
S 2-47
227 aut 25'142° 455/44
Nat Rubber
pure gum mix
Rings 44.8 x 38.6 mm
W0 = 740 - 1860 gr
L0 = 10 cm
MN 2331 VN 822/47 20'142°
Nat Rubber
pure gum mix
Rings 44.6 x 38.6 mm
W0 = 1080 - 1940 gr
L0 = 10 cm
MN 1986 VN 1/47 60'152°
Butyl Rubber I
pure gum mix
Rings 44.6 x 38.6 mm
W0 = 300 - 640 gr
L0 = 10 cm
MN 2234 VN 823/47 45'155°
Butyl Rubber II
pure gum mix
Rings 44.6 x 38.6 mm
W0 = 500 - 975 gr
L0 = 10 cm
%
m sec



against the contact breaker at C (Figure 1) without interrupting the discharging current for more than a fraction of a second. The rubber has then lost its energy by the impact, and it lies nerveless and loosely around the end-points A and C (Figure 1). In a few seconds, however, the ring has contracted

TABLE 2

SPEED OF RETRACTION AT HALF ELONGATIONS $S_{\frac{1}{2}}$ IN CM. PER SECOND AND SHORT-TIME PERMANENT SET λ_s IN PERCENTAGE FOR DIFFERENT RUBBERS AND TWO DIMENSIONS OF TEST-PIECES. DATA DETERMINED GRAPHICALLY FROM FIGURES 2 TO 12

Rings 22.7 × 28.7 × 1 mm.

Initial elongation		175%		200%		300%		350%		450%		500%		Impact resilience (Lüpke)
		$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	
Natural Rubber	A	—	—	—	—	—	—	13,000	—	14,000	—	—	—	84
	B	—	—	9,000	15	—	—	11,000	50	9,200	52	—	—	55
Hycar	A	—	—	3,800	50	—	—	6,600	100	—	—	—	—	17
OR-15	B	—	—	4,500	60	—	—	7,400	105	—	—	ca. 14,000	150	27
Hycar	A	—	—	5,200	40–60	10,000	55	—	—	—	—	—	—	38
OR-25	B	—	—	6,200	25	9,000	65	—	—	—	—	—	—	36
Neoprene	A	—	—	5,000	—	—	—	7,400	—	11,000	—	—	—	63
FR	B	—	—	8,000	—	—	—	14,000	—	14,000	—	—	—	53
Neoprene	A	—	—	5,000	25	—	—	7,000	ca. 70	8,500	75	—	—	63
G	B	—	—	—	—	—	—	8,000	—	10,000	60	—	—	50
Perbunan	A	5,400	22	—	—	—	—	—	—	—	—	—	—	47
	B	—	—	6,800	25	—	—	8,800	37	—	—	—	—	33
Butyl	A	—	—	2,900	37	—	—	6,000	55	7,300	—	—	—	13
	B	—	—	2,100	75	—	—	3,800	65	6,000	95	—	—	13
Butaprene	A	—	—	—	—	—	—	—	—	—	—	—	—	19
NXM	B	—	—	2,800	60	—	—	—	—	—	—	—	—	28
Buna-S	A	5,000	—	—	—	—	—	—	—	—	—	—	—	72
	B	—	—	5,200	48	—	—	12,000	58	14,500	70	—	—	43
Polymeth.	A	—	—	3,000	45	—	—	—	—	—	—	—	—	10
Homopol	B	—	—	3,600	45	—	—	5,500	70	—	—	—	—	10
Polymeth.	A	—	—	800	110	—	—	2,500	150	—	—	—	—	3
Copol.	B	—	—	600	140	—	—	1,900	210	3,400	235	—	—	3

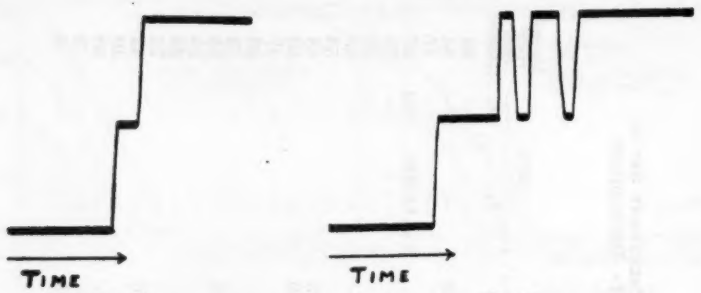


FIG. 13a. FIG. 13b.

FIG. 13.—Cathode oscillogram diagram at contacts K_1 and K_2 during opening. Figure 13a indicates a regular opening of K_2, that is, when K_1 opens the oscillogram light-beam jumps from the lowest level to the intermediate level, giving a short line during the short period of ring-retraction, and when K_2 opens the beam jumps to the highest level and stays there. Figure 13b shows a reclosing and reopening phenomenon of K_2, where the intermediate line jumps to the highest level and back again as noted in the text.

sufficiently to exert the force necessary to break the contact permanently. This moment is recorded in the right part of the curves. It does not give the real time of retraction, as the contact was opened and closed several times before that, owing to vibration in the device itself.

The same phenomenon is happening at higher final elongation; then, however, the time between the temporary and definitive opening of the contact is much shorter. This can be recorded in a cathode-ray diagram (Figure 13).

In the case of Figure 13 the total time of preambulatory openings of the contact can be estimated to be about 25 milliseconds. At still higher final elongations this interval disappears wholly and the real retraction time is measured.

For natural rubber this retraction speed is measurable to final elongations of almost zero. For synthetic rubbers, however, inflection points in the curves appear at easily measurable elongations. The times after this inflection point give no true record of the time elapsed. The horizontal part of the curves indicates the permanent set after a short time. Exactly speaking it indicates the elongation at which the stress is about 2.5 g. per sq. mm., *i.e.*, the force necessary to open the contact. The material tested can be characterized by two figures: (1) the speed of retraction, which can be estimated by taking the tangent of the retraction curve at about one-half of the original elongation; (2) the "permanent" set occurring after about 10 milliseconds (in the graph). In Table II these properties are listed; for comparison the impact resilience is also given. The short-time set can be compared with the permanent set measured in ordinary practice after 24 hours' elongation to 200 per cent (Table III).

Rings 36.7 × 44.7 × 2 mm.

Initial elongation		50%		75%		100%		150%		200%	
		$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s	$S_{\frac{1}{2}}$	λ_s
Natural Rubber	A	2,600	—	4,200	—	4,400	—	5,000	—	5,300	—
Butyl I	A	1,100	2	1,900	5	2,400	7	3,000	11	4,000	15
Butyl II	A	1,000	5	—	—	1,900	10	2,600	15	—	—
Hycar OR-15	A	1,300	12	2,000	20	3,300	30	4,000	37	4,200	50
		—	—	—	—	—	—	—	—	—	—
Neoprene	A	1,400	10	1,800	17	2,100	18	2,800	37	3,000	50

A = pure-gum vulcanizate. B = carbon black vulcanizate. Data calculated for an unstretched length of 10 cm.

TABLE 3

SHORT-TIME SET AND NORMAL PERMANENT SET OF DIFFERENT RUBBERS AFTER 200 PER CENT ELONGATION

A = pure-gum vulcanizate B = carbon black vulcanizate

		Short-time set after free retraction (%)	Permanent set after 24 hours' elongation 200% (in %)	
			Measured 1 hour after release	Measured 24 hours after release
Natural	A	—	3 to 5	1 to 2
	B	—	8 to 12	7 to 10
Hycar	A	50	6.5	2
OR-15	B	60	7	3
Hycar	A	40	6.5	2
OR-25	B	25	6	3
Neoprene	A	—	5	0.5 to 1
FR	B	—	3	0.5 to 1
Neoprene	A	50	18	5 to 7
GN	B	25	7.5	2.5
Perbunan	A	—	10 to 15	—
	B	25	5 to 15	—
Butyl	A	15 to 37	2	1.2
	B	75	11	7.5
Butaprene	A	—	6	3
NXM	B	60	7	3
Buna-S	A	—	5 to 10	—
	B	48	10 to 15	—
Polymeth.	A	45	2.5	0.5 to 1
Homopol.	B	45	7	5
Polymeth.	A	110	5 to 6	2 to 3
Copol.	B	140	12 to 13	6 to 7

Table II shows that in general the carbon black mixes have a higher set though their retraction may be more rapid. The ratio of speed of retraction of Butyl rubber and Hevea is (at 200 per cent) about 0.6 to 0.8, whereas the rebound ratio is about 0.2.

This can be understood only qualitatively in terms of the theory of the relaxation spectrum[6]. According to this theory the plastic-elastic behavior of rubber can be compared to a whole range (spectrum) of systems consisting of springs and dashpots in parallel coupled to an inert mass. Each unit is characterized by a modulus of elasticity and a relaxation time τ. Infinitely quick deformations only affect the springs and are wholly reversible. Slow deformations result in flow in the dashpots, and the reversible part of the deformation depends on the relaxation times of the unit. The stresses causing the deformation and the duration of the process determine which of the units will come into action.

The elongation in our experiments is a slow process (the rubber is relaxed during 1 to 2½ hours at room temperature); the retraction, however, is for the major part of the order of 5 milliseconds. The time of indentation and recovery during the impact resilience test is of the order of 12 milliseconds as determined by Mullins[7] for GR-S. The indentation in this case is no more than 0.35 cm., whereas in the retraction measurements movements of the order of 35 cm. are involved. So the movement on elongating the rubber for the retraction experiment is about 10,000 times slower than the indentation during the impact-resilience test. The free retraction, however, is about 100 times quicker than the recovery in the resiliometer.

The distribution of stresses in the rubber during the latter test is difficult to account for, as elongation, shear, and compression occur simultaneously.

The highest speeds recorded here are somewhat higher than those found by Stambaugh, Rohner, and Gehman[1], and Mrowca, Dart, and Guth[2], but on the whole, there is good agreement. An elastomer like Butyl rubber, though exhibiting low rebound, has still a reasonable speed of retraction.

Of all synthetic rubbers tested, Neoprene-FR most nearly approximates natural rubber with respect to its properties.

Table III shows that the set, measured after the free retraction, is much higher than the set measured in ordinary practice, though in the latter case the time of elongation at 200 per cent was much longer (24 hours against 2½ hours for the free retraction).

The extreme case is the copolymer of butadiene and methylpentadiene with a short time set of 110 per cent and a permanent set of 0.5 to 1 per cent.

THEORETICAL

Authors who have dealt with the theoretical problem of a freely retracting strip of elongated rubber have had considerable difficulty in coming to a realistic formulation of the rather complicated movement of the free end. James and Guth[3] gave the problem mathematical treatment.

Assuming Hooke's law to be valid, the free end on release immediately begins to move with a finite and constant velocity. Actually a somewhat different shape of the retraction curve is found.

The wave mechanism was clearly demonstrated by Stambaugh, Rohner, and Gehman[1] and Mrowca, Dart, and Guth[2] by means of high-speed photography. The rubber strip was divided in a great many parts by equidistant lines; the change of distances between these lines can be easily followed from the photographs, and is a measure for the differential elongation. Wildschut[3], on the other hand, introducing an "effective mass," calculated the movement of the free end on the assumption that all of the strip begins to retract at the moment this end is set free, and no internal friction is present.

The situation in simplified form is such that, as soon as the one end of the rubber is set free, a wave mechanism carries the impulse through the strip to the other end.

For the sake of simplicity a constant modulus (Hooke's law) is used. In absence of friction the wave velocity in space is $+ 1) (\lambda \sqrt{\frac{M}{\rho}}$ (1) according to classical oscillation theory.

The displacement of the tip is $\frac{\lambda}{\lambda + 1}$ times the distance covered by the wave impulse, so its velocity is:

$$V_t = \lambda \sqrt{\frac{M}{\rho}} \quad (2)$$

λ = elongation = $\frac{L - L_0}{L_0}$

M = modulus

ρ = density

L_0 = unstretched length

L = stretched length

For an unstretched length L_0 at elongation λ, the time for complete snap-back is:

$$t_e = \frac{\lambda L_0}{\lambda\sqrt{\frac{M}{\rho}}} = L_0\sqrt{\frac{\rho}{M}} \quad (3)$$

According to Equation (3), t_e is independent of the elongation if a constant modulus is assumed.

Figure 11 shows that this is surely not the case at elongations below 200 per cent. At higher elongations there is little difference for Hevea pure-gum vulcanizate (Figure 2).

For small elongations the stress-strain curve can be expressed by the formula:

$$\sigma = C\left(\alpha - \frac{1}{\alpha^2}\right) \quad (4)$$

σ = elastic tension

$$\alpha = \frac{L}{L_0} = 1 + \lambda$$

C = constant

Application of (4) leads to a higher modulus of elasticity for lower elongations than the assumed constant value. At the highest elongations the modulus increases again, due to the stiffening effect of crystallization. As the wave velocity is proportional to the square root of the modulus, t_e first increases and then decreases with elongation.

It has been pointed out by James and Guth[5] that, in this case, the wave impulse is no longer of fixed form. Mrowca, Dart, and Guth[2] showed with stylus experiments that, as a result of this effect (and frictional effects), the tip of the rubber moves with a higher velocity than, for instance, the middle point, after the wave impulse has passed. When additional friction forces are of importance it becomes difficult to give exact calculations for the retraction[1]. In Stambaugh's experiments it can be observed that the wave front is so much broadened that the differential elongation at the fixed end is lower than the initial elongation long before the impulse reached this end. As a certain permanent set appears to be present the ratio of tip velocity and wave velocity is no longer $\frac{\lambda}{\lambda + 1}$ but $\frac{\lambda - \lambda^1_s}{\lambda + 1}$. The velocity of the tip is then approximated by:

$$V_t = \sqrt{\lambda(\lambda - \lambda^1_s)\frac{M}{\rho}} \quad (5)$$

Here λ^1_s indicates the elongation at which the rubber is for the first time without tension; λ^1_s cannot be measured exactly as it is a function of time and, therefore, also of dimensions of the sample. However, $\lambda^1_s > \lambda_s$, as the recovery after elongation is approximately linear with the logarithm of time. By introducing $(\lambda - \lambda_s)$, a better correlation with the experiment is to be expected. Especially in case of carbon black mixes and after longer relaxation times, λ_s has an important effect on the velocity. However, the simplifications in the mathematical treatment may be prohibitive for exact agreement. It would be of interest for the theory of relaxation[7] to know the function of stress and elongation with time immediately after elongation and free retraction.

The foregoing measurements can be considered as a preliminary to the study of this subject.

CONCLUSIONS

The speed of retraction does not give the same proportionate number between a "quick" and a sluggish material as does the impact resilience. The latter property shows more pronounced differences.

Most rubbers after retraction exhibit a considerable amount of "permanent" set. This set measured at a short time after free retraction is considered as an auxiliary value for judging the elasticity of a material. Expressed in terms of speed of retraction and short-time set, the most elastic pure-gum compound measured was natural rubber, followed by Neoprene-FR. Polymethylpentadiene copolymer proved to be the last in the series. Of the carbon black mixes, Neoprene-FR proved more elastic than NR, probably due to a lower percentage of carbon black and the absence of Nurac (mineral rubber), of which the natural rubber compound contained about 10 per cent.

SUMMARY

The speed of retraction of the ends of elongated rubber rings relative to each other for a number of elastomers was measured at room temperature by a comparatively simple method. The results, plotted as elongation vs. time curves, indicate that the mechanism of retraction is complicated and cannot be described by a simple mathematical equation. In the present case the so-called permanent set plays a part in the retraction velocity. A mathematical equation is given to account for this phenomenon. Elasticity is judged in terms of speed of retraction and permanent set.

ACKNOWLEDGMENT

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THE MEASUREMENT OF STRESS RELAXATION OF UNVULCANIZED RUBBER BY MEANS OF THE MOONEY SHEARING-DISC VISCOMETER *

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In the vulcanized rubber product, it is the elastic characteristic that is most interesting and valuable. To the manufacturer of rubber products, however, the plastic properties of the unvulcanized or raw rubber, whether natural or synthetic, are equally important and interesting. In fact, elasticity in raw rubber is undesirable, and heavy machinery using a large amount of power is used to break this "nerve" so that such processes as calendering and extruding can be carried out successfully and uniformly.

The measurement and control of what is called, for want of a better word, plasticity, has become very important, and there is considerable literature on the subject. Apart from extrusion plastometers, which are not widely employed, the two types in use today are the compression or parallel-plate type and the shearing-disc instrument based on the design of Mooney[1].

The former method involves compressing a sphere or pellet of the rubber under examination between platens under a steady load and observing the degree of deformation that takes place. The instruments used take several forms, and there is unfortunately little if any standardization; platen sizes, pellet sizes, loads, time, and so on, have varied considerably. Furthermore, the methods of expressing results have varied; sometimes the thickness after a certain time is quoted, sometimes the time to compress from one thickness to another, and sometimes a softness figure calculated as a ratio of the deformation to the initial height, etc. The method has certain disadvantages (not insuperable but apparent in contrast to the Mooney instrument referred to later) of which the following may be mentioned. The rubber needs to be in a thick sheet from which a pellet of the required dimension and weight can be cut. The pellets are required to be fairly accurate for dimension. Distortion of the pellets often occurs during warming. There is, however, one great advantage, namely, that observation of the recovery of the sample towards its original shape after deformation can be made.

The shearing-disc plastometer measures, by means of the deflection of a calibrated spring, the force required to shear the rubber between two discs, one stationary and the other rotating at constant speed. The force depends on the effective viscosity of the rubber at the rate of shear employed. The original instrument described by Mooney[1] is more or less standard; a modified shape of rotor to give a uniform rate of shear throughout the specimen has been described by Scott[2].

This instrument has several advantages; no special shaped piece of rubber is required, since the sample is died out by the top and bottom stator plates,

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the working that the rubber receives removes any thixotropic effect, and changes with time can be followed. There are other points which need not be discussed here; they are listed by Mooney in his original paper.

The disadvantage, however, lies in the absence of any obvious method of recording the recovery. In a recent paper Scott[3] referred to the possibility of performing "recovery" measurements by stopping the rotor and observing the stress decay in the specimen as indicated by the gauge that measures the torque[4]. It is the object of this paper to discuss some work carried out in pursuit of this idea and to furnish data not given by the direct Mooney viscosity figure.

The requirements of processing are smoothness of calendering and extrusion and low and uniform shrinkage of the rubber. Both these features suggest that the extent of recovery after deformation, rather than the amount of deformation under a given load, would be the more important. In actual practice, with natural rubber and natural rubber compounds it was commonly found that simple softness measurements, *i.e.*, amount of deformation after a given time

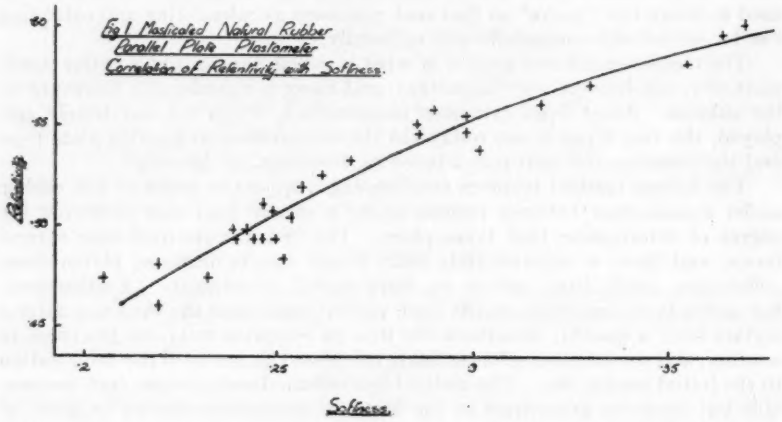

FIG. 1.

under a steady load, were sufficient for control purposes. The explanation of this lies in the fact that the breakdown of the rubber during mastication produces both a softening effect and a reduction in recovery. Measurements carried out on a parallel-plate plastometer, using pellets 1 cm. high and 1 sq. cm. cross-section under a load of 1 kg. for 30 seconds between platens 1 sq. cm. cross-section, with a recovery period of 30 seconds with the load off, showed that there was a good correlation between retentivity $R\left(=\frac{L_0 - L_2}{L_0 - L_1}\right)$ and softness $S\left(=\frac{L_0 - L_1}{L_0 + L_1}\right)$, where L_0 is the initial height, L_1 is the deformed height and L_2 is the height after recovery. This relationship applied in the case of measurements on a single batch and also between measurements on production batches. The ability of simple softness tests to forecast factory behavior involving recovery after deformation is, to a large extent, explained (See Figure 1).

In the case of GR-S, there is evidence that such a relationship does not, in fact, operate, for differences arise on account of variability of the raw material, processing technique, etc. The advantages of the shearing-disc viscometer as a practical rapid test to be carried out by semiskilled operatives made an instant appeal, and it was adopted in many laboratories in the rubber industry at a time when the large-scale conversion to synthetic (GR-S, butadiene-styrene copolymer) rubber was being made and the variability of the raw rubber appeared to render "plasticity" testing more important.

For the smooth extrusion of the rubber compounds based on GR-S, certain limits were set for the viscosity figure of batches of mixed rubber to be released for production; these limits were set by practical trial and any material showing a figure above standard was returned for reworking (remilling) to reduce its viscosity.

For some time this method of control seemed moderately reliable and adequate, but with a change in raw material and changes in the processing outside the control of the laboratory (but no change in the composition of the compound), it became evident that the viscosity limits were ineffective and, moreover, two batches of the same Mooney viscosity behaved very differently as regards smoothness and shrinkage after extrusion. In other words the softness or viscosity figure was not related to the recovery figure as in the case with natural rubber.

TABLE 1

SHEARING-DISC VISCOMETER: VISCOSITY AND "RECOVERY" VALUES

		Raw GR-S	GR-S compound Batch A	GR-S compound Batch B	Raw natural rubber
Viscosity value	V (3 min.)	34	41	38	94
Recovery value at					
10 sec.		16	13	11.3	59
20 sec.		13.3	11	9.2	57
30 sec.		12.0	10	8.3	47.5
45 sec.		10.9	9.2	7.7	44
60 sec.	R	10.1	8.7	7.1	41.6
120 sec.		8.5	7.6	6.0	35
V/R		3.36	4.72	5.35	2.26

Confirmation was provided by parallel-plate plastometer tests, but the future use of the Mooney instrument (which was expensive and, in any case, had already made its appeal because of simplicity and speed of operation) had to be considered. It was decided to investigate fully the possibility of doing stress relaxation measurements on the Mooney instrument on the lines of Scott's suggestion.

After the normal determination of Mooney viscosity (V) at 100° C after three minutes' running[5], the motor was switched off, and the decay of the gauge reading was recorded at intervals, with results as shown in the case of several samples (Table 1). It seemed reasonable to standardize on 1 minute, and the "recovery" figure (R) after this time was taken for correlation with processing behavior. Initial difficulties in reproducing the figures were overcome by the fitting of a small electrical vibrator to the gauge to eliminate any tendency to sticking, and by repeating tests, *i.e.*, restarting and restopping the motor to obtain 2 or 3 values for R from the same specimen and averaging.

TABLE 2

SHEARING-DISC VISCOMETER; VARIATION OF VALUES OF V AND R WITH TIME OF STORAGE AFTER MIXING; NATURAL RUBBER

Time after mixing (hours)	Batch A			Batch B		
	V	R	V/R	V	R	V/R
1	71	11.2	6.3	77	10.5	7.3
3	74	11.8	6.3	75	11.3	6.7
22	76	11.9	6.4	75	10.7	7.0
70	76	11.3	6.8	73	12.2	6.0
96	77	13.1	5.9	76	13.3	5.7
110	73	12.2	6.0	77	13.2	5.8
134	79	12.7	6.2	78	13.1	6.0
150	78	12.3	6.3	79	12.7	6.1
157	79	12.8	6.2	78	12.4	6.3
398	79	12.9	6.1	78	11.8	6.6
442	77	12.1	6.4	—	—	—

It was obvious from the preliminary work that there were differences to be shown up by this technique, but it was necessary to relate V to R for it to have any practical value. The ratio V/R seemed logical and was adopted.

At this stage it is convenient to consider what happens under the conditions of this test. The rotor is driven through a worm and pinion, the latter being mounted on the rotor shaft, and the former on a shaft free to move longitudinally in its bearings but its travel opposed by a leaf spring. As the rotor turns in the rubber, thereby shearing it, the rubber exerts an opposing torque on the rotor, which in turn transmits a thrust to the worm shaft; the spring is deflected, and the deflection is registered on a dial guage. When the motor is switched off, the torque on the rotor is less, but still in the same direction. If the rubber shows a tendency to complete recovery from deformation, the torque remains high and the reduction in dial reading is relatively small; that is, a high figure for R or a low figure for V/R indicates a low rate of stress decay and, therefore, high shrinkage and roughness on calendering or extruding.

Practical trial of production batches showed a good degree of correlation, and limits for V/R could be fixed. The following additional experimental data are of interest.

Effect of storage on V and R figures.—It is well known that there are thixotropic effects in unvulcanized rubber, and tests on the parallel-plate instruments show some increase in hardness with time after milling or mixing. Due to the working that the rubber receives in the shearing-disc instrument, these

TABLE 3

COMPARATIVE PLASTICITY TESTS ON 10 RUBBER COMPOUNDS

Composition	Parallel-plate			Shearing-disc		
	Softness	Retentivity	Plasticity	V	R	V/R
Natural rubber (A)	.231	.525	.121	80	12.6	6.35
Natural rubber (B)	.208	.449	.096	74	12.2	6.05
Natural rubber (C)	.300	.622	.186	60	6.5	9.25
Natural rubber (D)	.338	.581	.196	66	7.8	8.45
Natural rubber (E)	.220	.563	.124	80	11.9	6.70
Natural rubber/GR-S	.335	.462	.155	54	6.4	8.45
GR-S (A)	.285	.405	.118	52	9.5	5.50
GR-S (B)	.122	.310	.038	92	17.3	5.30
Neoprene (A)	.373	.659	.246	47	4.2	11.20
Neoprene (B)	.314	.520	.163	54	6.0	8.95

thixotropic effects are removed, and no very significant changes in the V and R figures occur (see Table 2).

Comparison of parallel-plate and shearing-disc values.—Data were obtained on some ten compounds, based on natural rubber, GR-S and Neoprene, on both instruments, and the results are given in Table 3. In the case of the parallel-plate plastometer, the softness and retentivity were calculated according to the formulas given. In addition, the plasticity[6] obtained by the product of softness and retentivity, *i.e.*, $(L_0 - L_2)/(L_0 + L_1)$, is given. In the case of the shearing-disc instrument, the direct viscosity reading at 3 minutes (V), "recovery" after 1 minute (R), and ratio V/R are given.

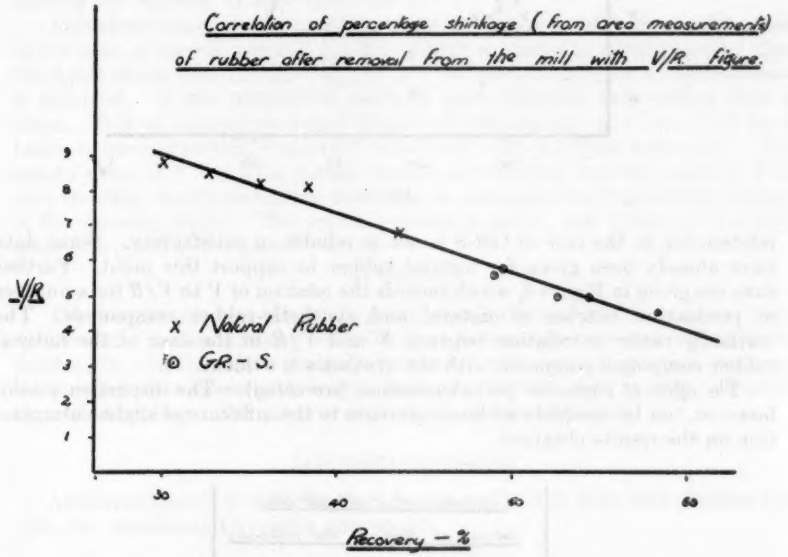

FIG. 2.

There is fair correlation between parallel-plate softness and shearing-disc viscosity. Scott and Piper[7] have shown that different types of stock give somewhat different correlations between shearing-disc and parallel-plate instruments. The explanation lies in the wide differences in the mean rates of shear in the two instruments. There is correlation also between parallel-plate plasticity and shearing-disc V/R which has already been referred to and is borne out on production trials.

Comparison of shrinkage of rubber after removal from mill with V/R figure.—An attempt was made to correlate the percentage shrinkage (from area measurements) of a sheet of rubber on removal from the laboratory mill with the V/R figure. A series of measurements was made with varying times of milling on both a natural rubber and a GR-S compound of similar type. The data, given in Figure 2, show good correlation. How far the same correlation holds for compounds of different type has yet to be ascertained.

The relation of V to V/R.—Reference has been made above to the fact that softness and recovery are related in the case of natural rubber but that such

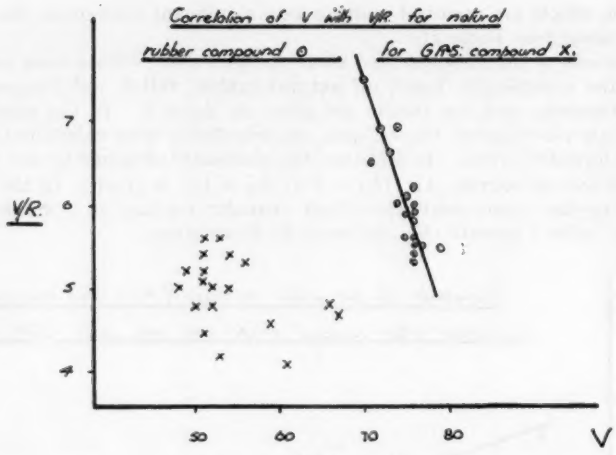

FIG. 3.

relationship in the case of GR-S is not so reliable or satisfactory. Some data have already been given for natural rubber to support this point. Further data are given in Figure 3, which records the relation of V to V/R for a number of production batches of natural and synthetic-rubber compounds. The markedly better correlation between V and V/R in the case of the natural rubber compound compared with the synthetic is evident.

The effect of partial or prevulcanization (scorching).—The discussion would, however, not be complete without reference to the influence of slight vulcanization on the results obtained.

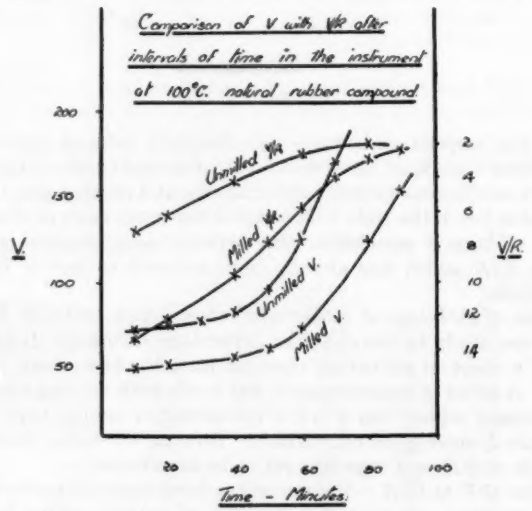

FIG. 4.

Depending on the type and amount of the accelerator, and the temperature, rubber during processing undergoes some degree of vulcanization. The extent of this vulcanization varies through a very wide range, but normally does not seriously affect calendering, extrusion, etc. There does, however, come a time when the material is in such a state of partial or prevulcanization that it shows excessive shrinkage and roughness on extruding or processing; it is then said to be scorched.

There can, therefore, be two causes of roughness and shrinkage, lack of breakdown and prevulcanization. It is usual to follow the tendency of a particular compound to prevulcanize by observing the plasticity changes on heating the material at 100° C or 120° C.

This observation can be made on either instrument, and it is usually found in the case of simple softness (parallel-plate) or viscosity (shearing-disc) that the figure shows little change until, after a certain critical time, a rapid increase is observed. If the material is partially prevulcanized, this critical time is short. It is of interest to record (Figure 4) the changes of V and V/R for a batch of natural rubber compound before and after a milling treatment. The steady value of V until the critical point is to be noted, but the value of V/R rises steadily, clearly indicating the onset of vulcanization without any change in the viscosity figure. The milled material is softer, and it also gives a very much increased V/R figure.

SUMMARY

The measurement of the tendency of unvulcanized rubber to recover from deformation on the Mooney shearing-disc viscometer has been found to be practicable, and the results correlate fairly well with recovery measurements on the parallel-plate plastometer and shrinkages of rubbers after milling, calendering and extruding. Partial prevulcanization is also indicated.

ACKNOWLEDGMENT

Acknowledgment is made to the laboratories of the John Bull Rubber Co. Ltd., for permission to publish this paper.

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[2] Scott, *J. Scientific Instruments* **22**, 206 (1945).
[3] Scott, *Trans. Inst. Rubber Ind.* **20**, 15 (1944).
[4] Recently Macdonald (British patent 578,496) described a modification of this viscometer, which involves an arrangement designed to make possible free rotation of the outer chamber of that apparatus, to determine recovery.
[5] The sample of rubber is prewarmed for 15 minutes in an oven at 100° C.
[6] The expressions for softness, retentivity, and plasticity are those used by Karrer, Davies, and Dieterich (*Ind. Eng. Chem. Anal. Ed.* **2**, 96 (1930)). Their definition of plasticity as the susceptibility to, and retentivity of, deformation leads to the formula given. This method of measurement and its expression has much to recommend it. A low plasticity (from a practical viewpoint, poor processibility) can arise from a high recovery from deformation (large L_2 value) or from a small deformation (large L_1 value).
[7] Research Association of British Rubber Manufacturers, Report No. 216 (Mar. 28, 1944); RUBBER CHEM. & TECHNOL. **18**, 877 (1945).

SOME NEW COMPOSITIONS BASED ON CONDENSATION RUBBERS *

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When roughly equivalent weights of a dibasic acid and a glycol are heated together, water is eliminated and linear polymeric materials are formed:

$$\text{—R—COOH} \quad \text{HO—R}_1\text{—OH} \quad \text{HOOC—R—COOH} \quad \text{HO—R}_1\text{—}$$

$$\text{—R—C(=O)—O—R}_1\text{—O—C(=O)—R—C(=O)—O—R}_1\text{—O—C(=O)—R—C(=O)—O—R}_1\text{—}$$

$$+ \ H_2O \qquad +H_2O \quad + \quad H_2O \qquad + \ H_2O \qquad + \ H_2O$$

The properties of the polymers vary over a wide range, according to the components used and the molecular weight and structure of the chains. Some are viscous oils, some hard crystalline materials with melting points as high as 100° C, some are fiber-forming, while others have rubbery properties. Considerable progress has been made in correlating molecular structure with physical properties, and knowledge of the influence of the various component acids and glycols on molecular configuration and ultimate physical properties has increased greatly in recent years[1].

Several rubbery polymers have been described, one of which occurs naturally[2] and a few of which are already being manufactured in bulk. It is significant that at this early stage in the development of this class of polymers, rubbers with widely different physical properties have been obtained. For example, Vulkollan-N has a much higher tensile strength and tear resistance than natural rubber[3], Paraplex S.200 is claimed to be highly heat resistant[4], and Vulcaprene-A is more resistant to gasoline than any other rubber, and also is of particular value in the leathercloth industry[5].

It is becoming clear that one of the advantages of condensation rubbers lies in the ease and precision with which the molecular configuration can be altered by variation of the components and the methods employed to obtain high molecular weight. For rubbery properties, certain conditions must be fulfilled[6], and in the case of Vulcaprene-A these have been met in the following manner.

(1) A high molecular weight (higher than for fibers) has been achieved by carrying out the condensation in two stages. First, the preparation of a wax or molecular weight of approximately 5000 by straightforward elimination of water; secondly, reacting the terminal groupings of this wax with a diisocyanate[7] to carry the molecular weight well up into the rubber range.

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(2) The crystallite melting point is low by reason of the polyester structure, and is further reduced by interpolymerization. Vulcaprene is a polyester amide made from ethyleneglycol, monoethanolamine, and adipic acid.
(3) The second-order transition temperature is low, owing to the predominantly polyester chain. The number of amide links is kept low to avoid an increase in this temperature.
(4) Cross-linking sites are provided by the amide groupings, which are capable of reacting with formaldehyde liberating agents[8], polyisocyanates, or with certain dichromates[9], to give a cross-linkage very similar in its influence on physical properties to the effect of sulfur on rubber, or tanning agents on leather. The formaldehyde-liberating curing agent most suited to Vulcaprene is a complex amine-formaldehyde condensation product—Vulcafor-VHM—which is catalyzed by an accelerator, Vulcafor-VDC (a halogenated naphthol), when heated. The polyisocyanate, Vulcafor-VCC, is used as the room temperature curing agent.

Vulcaprene can be compounded and press-cured with these curing agents in the same way as natural rubber, but much more important uses have been found from an investigation of its compatibility with other high polymers. It appears to function as a novel vulcanizable polymeric plasticizer, producing mixtures which have particular value in the spreading industries. A brief description of the properties of these mixtures is given below.

TABLE I

HARDNESS OF VULCAPRENE/POLYVINYL FORMAL MIXTURES (CURED)

Polyvinyl formal (%)	50	30	20	10
Vulcaprene (%)	50	70	80	90
Shore hardness	96	82	63	48

When finely divided polyvinyl formal is added to Vulcaprene on a rubber mill and the temperature is raised to 120° C, the opacity due to the polyvinyl formal disappears as the polymer merges with the Vulcaprene, and finally a homogeneous leathery sheet is obtained. The two polymers are compatible in all proportions, and the products vary from soft rubbery materials when the proportion of Vulcaprene is high to a hard brittle material when the proportion is low. Similar results are obtained when the mixtures are prepared in solution.

During the incorporation of the formal by milling, some formaldehyde is liberated, so there is the possibility that partial curing of the Vulcaprene takes place. The degree of cure must be slight, however, as at this stage the product is still thermoplastic and soluble. When the normal formaldehyde-liberating curing agents are added and the compound is heated, proper cure of the Vulcaprene takes place and the product is no longer thermoplastic[10].

The Vulcaprene-formal mixture can be made into a dough with solvents such as benzene-alcohol or ethylene dichloride, and these doughs can be spread onto cloth in the conventional manner. In the uncured condition, the coating is flexible and fairly tough, but is thermoplastic. When cured it becomes abrasion-resisting, flex-resisting, and nonthermoplastic. The most useful proportion of Vulcaprene to polyvinyl formal appears to be in the region of 70 parts of Vulcaprene to 30 parts of formal. Leather cloths based on coatings having this composition have excellent abrasion- and flex-resistance, and

samples have been prepared having a scrub-resistance of 40,000 cycles, compared with the 250 cycles for the nitrocellulose and the vegetable oil types of coating. Unfortunately the fact that satisfactory doughs can be prepared only in chlorinated solvents has prevented large-scale development of this coating composition, apart from certain very stiff types of gasoline-resisting diaphragm material.

Admixtures of Vulcaprene with many of these high polymers increases its hydrolytic stability and improves its resistance to hot humid conditions. This effect is also experienced with the other high polymers referred to later.

Vulcaprene and nitrocellulose are also compatible in all proportions. The products vary from brittle solids, where the proportion of nitrocellulose is high, to soft flexible rubbery products, where the proportion of Vulcaprene is high. While incorporation can be achieved on the rubber mill, it is much safer to carry out the mixing in solution. The whole range of mixtures is thermoplastic, but, as would be expected, the softening point rises with the proportion of nitrocellulose. They are rendered nonthermoplastic by heating with the formaldehyde-liberating curing agents[11], or by interaction with the cold-curing polyisocyanate. The heat-curing agents are of only academic interest here, as the heating of films containing nitrocellulose is a hazardous operation not suitable to bulk production. Films of Vulcaprene-nitrocellulose mixture that have been cured in this way, although hard and nonthermoplastic, are very brittle where the proportion of nitrocellulose exceeds 50 per cent. This may be due to some interaction between the nitrocellulose and the formaldehyde-liberating agents, but it is more likely to be simply an embrittling effect, due to exposure of the nitrocellulose to a temperature of 120° C.

TABLE II

PROPERTIES OF VULCAPRENE–NITROCELLULOSE MIXTURES

Nitrocellulose (%)	20	40	50	60	80
Vulcaprene (%)	80	60	50	40	20
Uncured	Soft and sticky	Pliable but thermoplastic	Pliable but not rubbery	Resilient and tough	Resilient and hard
Heat cured	Tough and rubbery	Very tough; low tear	Very tough and hard	Very hard and brittle	Very hard, very brittle
Cold cured	Fairly tough and rubbery	Tough; rubbery; inextensible	Tough, rubbery, inextensible	Hard and tough	Very hard and brittle

Where curing is carried out with the polyisocyanate, the products are nonthermoplastic, and brittleness appears where the proportion of nitrocellulose is 75 per cent. In this case the polyisocyanate reacts with the nitrocellulose.

These mixtures can be spread onto fabric from a dough made using acetone-ester mixtures. The preparation of the dough, spreading, and embossing present no unusual features.

As would be expected, the flexing-resistance falls off as the proportion of nitrocellulose increases and, in the case of the uncured mixtures, when the coating contains sufficient Vulcaprene to have a reasonable flexing life, it is soft and even slightly tacky. When curing has been carried out, this is not the case, and a coating containing about 25 per cent nitrocellulose has a scrub value of about 5000 cycles and has a tack-free, abrasion-resisting surface. Its properties are inferior to those of some of the other coating compositions described in this paper.

Vulcaprene is also compatible with cellulose acetate and, as in this case incorporation cannot readily be carried out on a rubber mill, it is necessary to

prepare the mixtures by solution methods. The two materials are not compatible in all proportions, and the products show definite signs of incompatibility where the amount of cellulose acetate exceeds 40 per cent. Films prepared from the mixtures are soft and rubbery when the proportion of cellulose acetate is low, but toughen as the proportion of cellulose acetate is increased to 40 per cent.

Thermoplasticity is removed when the mixtures are cured with the heat-curing agents, Vulcafor-VHM and -VDC, or the cold-curing agent, Vulcafor-VCC[11]. In both cases the curing agent reacts with the cellulose acetate, as well as curing the Vulcaprene, which may account for the toughness of the cured films.

The Vulcaprene-cellulose acetate mixtures can be made into a dough with acetone-ethyl acetate as solvent, and this can be spread on to cloth in the usual way. The process presents no novel features, and embossing is carried out in the conventional manner. The uncured coatings are thermoplastic when containing sufficient Vulcaprene to have good flexing properties, but after curing with either the formaldehyde-liberating agents or the polyisocyanate system,

TABLE III

PROPERTIES OF VULCAPRENE–CELLULOSE ACETATE MIXTURES

Cellulose acetate (%)	20	30	40	50	60
Vulcaprene (%)	80	70	60	50	40
Uncured	Soft and sticky	Rubbery but thermoplastic	Rubbery but thermoplastic	Pliable, inextensible*	Incompatible
Heat cured	Soft and rubbery	Pliable and tough	Very tough	Incompatible	Incompatible
Cold cured	Soft and rubbery	Tough and pliable	Hard and resilient	Hard and resilient *	Incompatible

* Shows signs of incompatibility.

promising coatings are obtained. The optimum composition appears to be 70 parts of Vulcaprene and 30 parts of cellulose acetate. Coatings of this type have scrub values in excess of 20,000, have a low coefficient of friction, and at the same time are resistant to scratching and abrasion. Leather cloths based on this type of film have given good practical service.

Vulcaprene is also compatible with degraded vegetable tanned leather. If disintegrated vegetable tanned leather scrap is boiled with water for about 30 minutes, a partial breakdown of its structure takes place, and a thermoplastic resinous material is formed which is compatible with Vulcaprene. Incorporation is achieved by adding the moist hydrolyzed leather to the Vulcaprene running on a mill; gradually the moist resinous material merges with the Vulcaprene, and when the water has been removed by heating, a tough leathery sheet is obtained. In the presence of benzene-alcohol, toluene-methylethyl ketone or toluene-acetone mixtures, a stiff dough can be produced, which can be spread using normal machinery. In the uncured condition the coating is not very attractive, for it is thermoplastic and soft, but when the formaldehyde-liberating curing agents are added and the material is cured in hot air, a tough flex- and abrasion-resisting coating is obtained[13]. In this case cure with a polyisocyanate cannot be used, owing to preferential reaction with the leather to give a brittle product of no value as a cloth coating.

As the proportion of leather is increased, the coating ceases to have the rubbery feel and characteristics of an all-Vulcaprene proofing, and it becomes harder and more abrasion-resisting, and has a lower coefficient of friction. The compounds containing between 45 and 52 per cent leather present the best compromise between abrasion resistance and flex and scrub resistance. With coatings of this type, scrub values in excess of 30,000 have been obtained, yet at the same time the abrasion-resistance is equal to the highest grade nitrocellulose coating—probably the most abrasion-resisting coating known to the industry.

Where the amount of leather exceeds 55 per cent, the products become harder and the flex resistance falls, and when the leather content reaches 60 per cent the scrub resistance is reduced below 1000.

In the manufacture of a leather cloth of this type, it is desirable to give the coating a composite structure by applying—

(1) an anchor coat containing 75 per cent of Vulcaprene to get a satisfactory key to the cloth without forcing the polymer into the fibers and causing stiffness;
(2) a main coat of Vulcaprene-leather mixture (roughly 1:1);
(3) a lacquer of Vulcaprene-cellulose acetate. This keys perfectly to the main coat and gives an attractive, easily colored drag-free surface to the leather cloth.

Typical formulations are given below.

Ingredients	Anchor coat	Main coat	Glossy lacquer	Dull lacquer
Vulcaprene-A	100	100	100	100
Hydrolyzed leather	45	100	—	50
Cellulose acetate	—	—	60	40
Tricresyl phosphate	5	10	—	—
Color	—	Up to 20	Up to 40	Up to 20
Vulcafor-VHM	10	10	10	10
Vulcafor-VDC	0.75	0.75	0.75	0.75

Products prepared on this basis have proved acceptable to the market by reason of their combination of high flexing and abrasion resistance and their drag-free surface.

Vulcaprene is also compatible with other degraded proteins such as glue and gelatin. These are incorporated by swelling them with a little water, adding to the Vulcaprene on a rubber mill, and allowing mixing to take place while the compound dries down under the influence of the heat from the rolls. As would be expected, where the proportion of Vulcaprene is low, the products are very easily affected by water, and even when the proportion of Vulcaprene is high, swelling by water causes a serious deterioration in properties. Cure is carried out by heating in the presence of the formaldehyde-liberating curing agents, and also by the use of a dichromate. In both cases it is probable that the Vulcaprene and the degraded protein react with the curing agent. Even so, the swelling in water is such as to limit the application of these materials.

Vulcaprene does not appear to form useful mixtures with polystyrene, polyvinyl chloride, polyvinyl acetate, polymethylmethacrylate, or polythene.

The mixtures of Vulcaprene and cellulose acetate are of particular interest, as it has been found that they provide an effective lacquer or polish for rubber proofings. It functions as an abrasion-resisting, and flex-resisting coating, which is of value in bringing the rubber proofing into the leather cloth market.

It is important to achieve a good bond between the lacquer and the rubber of the proofing. This is done by applying over the surface of the uncured proofing a "lick" of a solution of Vulcaprene and half its weight of a polyisocyanate in a solvent consisting of equal parts of aromatic hydrocarbon and acetone. By this means some of the polyisocyanate is carred into the rubber by the benzene, so not only does the isocyanate cure the Vulcaprene, but it reacts with the rubber to give a chemical bond between the Vulcaprene film and the rubber. The Vulcaprene-cellulose acetate adheres well to this interface. This technique can be used with natural rubber, GR-S, Neoprene, Perbunan, Hycar, and Butyl rubber, and will give good adhesion even under wet conditions.

The optimum proportion of cellulose acetate is between 28 and 33 per cent; less makes the lacquer too soft and imparts a relatively high coefficient of friction; more makes the lacquer brittle so that it cracks when severely flexed.

The cure is carried out by the use of a polyisocyanate, in which case no heating is necessary, provided, of course, the rubber mix cures at room temperature. On the other hand, where a heat cure is possible, the rubber mix is compounded for a dry heat cure of 1 hour at 125° C, and the formaldehyde-liberating agents are then used to cure the lacquer.

As an alternative, where it is desired to give a single coat of Vulcaprene-cellulose acetate, the polyisocyanate is used as curing agent, and the whole proofing cured for, say, half an hour at 125° C.

This type of lacquered rubber proofing is of considerable interest to the clothing and leather cloth industries. Where a leather cloth is being made, the rubber base should be as hard and as tightly cured as possible to give a good handle and a hard surface. When lacquered, the product has sufficient abrasion resistance for all except the most arduous conditions, and at the same time a scrub value of the order of 5000. The attraction of a product of this type is of course its cheapness, as it is based on a well filled natural rubber coating—and at the same time has a scrub and flexing life very much greater than the prewar leather cloths.

For clothing, the rubber is made as resilient as possible, while the lacquer is compounded to give a low coefficient of friction. Generally it is desirable to pigment the lacquer, as by this means very bright colors are obtained; where a dull matt surface is desired, a proportion of hydrolyzed leather is incorporated.

The Vulcaprene-cellulose acetate lacquer is also of value in the coating of paper. The lacquer (containing 25–30 per cent of cellulose acetate) is applied by spreading, and is cured at room temperature by the incorporation of a polyisocyanate. It can, like most coated papers, be embossed to give a very clear imprint, and has a valuable combination of abrasion and flex resistance. It shows promise in such applications as bookbinding.

The lacquer can be applied also with advantage to latex treated paper. Certain types of absorbent paper when treated with latex have a greatly enhanced tear resistance and a very leatherlike feel. When coated with the vulcaprene-cellulose acetate, a product is obtained which is abrasion- and flex-resistant and which has sufficient tear resistance to make it of great interest to the leather cloth industry.

These results show that the plasticizing of high polymers is not confined to simple monometric materials or even to low molecular weight polyesters. Vulcaprene-A (a rubbery condensation polymer) is capable of a considerable plasticizing action, and has the important advantage of being vulcanizable. It is shown, moreover, that where two high polymers are compatible, there is more than a simple plasticizing action and, in effect, the polymers mutually

modify their properties to give novel products which are of major interest to the spreading industries.

SUMMARY

By the condensation of a dibasic acid and direactive alcohol or amine, linear polymers are produced. Under certain conditions rubbery polymers are obtained, and a number of condensation rubbers with outstanding physical properties have been described. One of these, a diisocyanate-modified polyester amide (Vulcaprene-A) has been found to be compatible with nitrocellulose, polyvinyl formal, cellulose acetate, degraded vegetable tanned leather, gelatin, and glue. These mixtures can be vulcanized by formaldehyde-liberating agents used to cure Vulcaprene, and in most cases the curing reaction appears to take place not only with the Vulcaprene but with other high polymers.

Combinations of Vulcaprene and cellulose acetate and of Vulcaprene and degraded leather are of great interest to the leather cloth industry, as they can be spread on to cloth to give coatings with outstanding flex and abrasion resistance.

The Vulcaprene-cellulose acetate mixture is of value also as an abrasion- and flex-resisting coating for rubber proofings to give products which, while cheap to produce, are likely to give superior service to prewar leather cloths. This type of coating can be applied also to paper.

The diisocyanate modified polyester amide behaves not only as a novel vulcanizable polymeric plasticizer, but, in combination with these high polymers, gives new products of major interest to an important branch of the rubber industry.

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STRUCTURES IN RUBBER REËNFORCED BY CARBON BLACK *

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INTRODUCTION

In a recent paper Mullins[1] discusses the effects of prestretching on certain properties of rubber vulcanizates containing colloidal carbon and other fillers. He concludes that any increased stiffness and electrical conductivity imparted by the fillers can be destroyed by flexing or stretching, and he attributes the softening to breakdown of chains or filler particles and adsorptive filler-rubber bonds. Mullins supports the view (to which one of the present authors formerly subscribed) that carbon particles flocculate in rubber. Ladd and Wiegand[2] have concluded that carbon chain structure, which is present in blacks before incorporation into rubber, largely persists after mixing and milling, a view which has received support from recent work of the present authors[3], who have also contested the theory that structure can be built up after the mixing process by flocculation or catenation of individual particles. The present research is concerned primarily with the nature of the bonds broken by stressing, and their contribution to the stiffness.

EFFECT OF STRESS ON STIFFNESS

The experiments were performed on a vulcanizate having the following composition by weight: smoked sheet 100, Statex-K 50, zinc oxide 5, stearic acid 3, mercaptobenzothiazole 0.5, and sulfur 3. Statex-K was chosen as a typical example of an ultrafine furnace black which possesses considerable chain structure and imparts high reinforcement and electrical conductivity to rubber. The test-piece, of dimensions $10 \times 0.3 \times 0.3$ cm., was suspended, together with an attached scale pan, in front of a millimeter ruler. Changes in the length of the specimen were determined by means of two marks, initially placed 5 cm. apart.

The softening which takes place when a rubber-black vulcanizate is stressed may be studied by subjecting the test-piece to fixed stretches or to fixed stresses, *i.e.*, by making either elongation or stress the independent variable. In these experiments stress was chosen as the independent variable, since it is most likely to determine any structural breakages.

The following procedure was adopted. Add w_1 kg., note the elongation, remove weight, and note the permanent set after standing for 15 minutes. Read w_1 kg., followed by w_2 kg., noting the extension in each case. Remove all weights and read the permanent set after 15 minutes. Read w_1 kg. and w_2 kg., followed by w_3 kg., noting the elongation in each case. This procedure is repeated with progressively increasing loads, so that measurements of the stiffness at several stresses and after various prestresses are obtained. Owing to

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set effects nominally constant stresses are not quite constant, but this is a secondary effect, and the values entered on the graphs are those of the mean stresses.

The effect of stress in softening the rubber-carbon vulcanizate is shown in Figure 1, where the percentage elongation of the test-piece, at several stresses and for a range of prestresses, is plotted against the prestress. There is a linear relation between the extension and the prestress within the range studied. This enables an interesting deduction to be made. The dotted lines in Figure 1 pass through imaginary points for prestresses less than the stress used to determine the stiffness. These are the values which would be obtained if the stiffness could be measured without stressing the specimen. It follows that the intercepts of the dotted lines with the axis of zero prestress are the percentage elongations which would have been obtained before prestressing, if the stressing

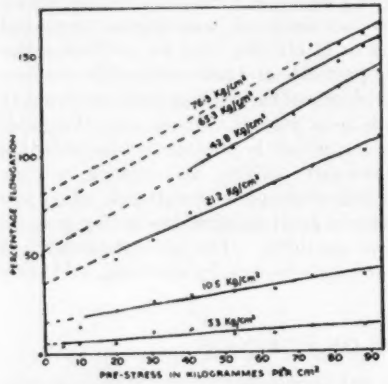

FIG. 1.—Relation between percentage elongation and pre-stress for a rubber vulcanizate containing 50 parts Statex-K black.

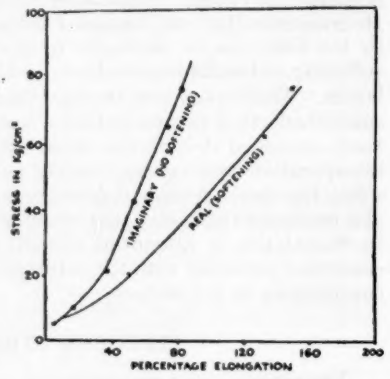

FIG. 2.—Stress-strain relationship.

had not caused softening. The actual and imaginary stress-strain curves are shown together in Figure 2.

EFFECT OF STRESS ON CARBON CHAIN STRUCTURE

It is clear that changes in the number of carbon-carbon contacts in rubber compounds alter the specific resistance by making or breaking conducting paths. The history of the carbon-carbon system was therefore studied by measuring the electrical resistance of the samples 15 minutes after each prestress, *i.e.*, in the relaxed condition, before each determination of stiffness. The technique used has been described in a recent paper[3].

Figure 3 shows the increase of the specific resistance of the vulcanizate with prestress. The effect is similar to that in unvulcanized rubber[3]. The curve rises steeply at first and then flattens. An experiment with another test-piece, in which the stress was increased to the breaking point, confirmed the trend and showed a maximum resistivity much lower than that of a pure rubber vulcanizate, which is about 10^{15} ohm-cm. This indicates that a considerable part of the structure of Statex-K remains, no matter how severely the specimen has been stressed, and suggests that breakage of carbon chain structure is not the

main reason for the softening effect. But it can be objected that the logarithm of the specific resistance may be less sensitive to changes in structure when the structure is diminished, and it is, therefore, desirable to interpret the resistance changes quantitatively in terms of contacts between particles.

In a forthcoming paper[4], Blanchard shows that the change in specific resistance (R) with degree of structure (n) is given by the equation:

$$\frac{1}{R}\frac{dR}{dn} = -\frac{\gamma(1-F)}{n} \tag{1}$$

where n = mean number of particles per chain, F = the (constant) weight concentration of carbon black expressed as a fraction of the total weight of rubber and other ingredients, and $\gamma = 25.4$ according to the data at present available.

Integrating (1) we obtain:

$$-\int_{R_o}^{R}\frac{dr}{R} = \gamma(1-F)\int_{n_o}^{n}\frac{dn}{n}$$

which gives:

$$\frac{n}{n_o} = \frac{(R_o)^{1/[\gamma(1-F)]}}{(R)} \tag{2}$$

where n_o and R_o are, respectively, the total structure and specific resistance before the vulcanizate is stressed, and n and R are their values after stressing.

In Figure 4 the mean number of particles per chain expressed as a fraction of the number before stressing, *i.e.*, the ratio $\frac{n}{n_o}$ obtained from Equation (2), is plotted against the prestress. The curve appears to be exponential in type, and there is apparently an asymptote roughly in the position marked XY on the graph, representing the part of the structure which is unaffected by stressing, and which can be termed the subpermanent structure n_p. The temporary structure n_t is the part which is affected by stressing. We may, therefore, write: $n = n_p \times n_t$, since it can be shown that the total mean number of particles per chain is the product of the mean values for the components.

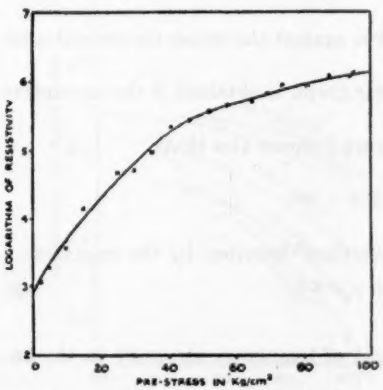

FIG. 3.—Effect of prestress on the resistivity of an unstressed rubber vulcanizate containing 50 parts Statex-K black.

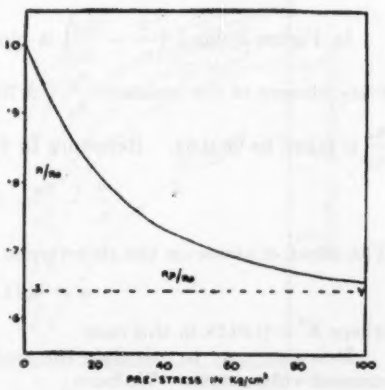

FIG. 4.—Effect of prestress on the mean number of particles per chain, expressed as a fraction of the initial value.

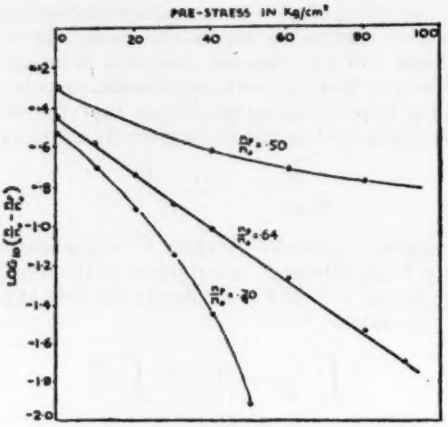

FIG. 5.—Decay of temporary structure with prestress; amount of subpermanent structure n_p.

It is now possible to determine the asymptote, *i.e.*, $\frac{n_p}{n_o}$. The temporary structure n_t cannot be less than unity, since $n = 1$ is the condition for discrete particles. Writing $n_t = 1 + \tau$, where τ is the mean number of temporary contacts per chain we have:

$$\frac{n}{n_o} = \frac{n_p(1 + \tau)}{n_o}; \text{ hence } \frac{n}{n_o} - \frac{n_p}{n_o} = \frac{n_p\tau}{n_o}.$$

Suppose there is a simple exponential law for the breakage of temporary contacts with stress. Then $\tau = \tau_o e^{-KS}$, where K is a constant and S is the stress.

Hence

$$\log\left(\frac{n}{n_o} - \frac{n_p}{n_o}\right) = \log \frac{n_p}{n_o}\tau_o e^{-KS}.$$

In Figure 5, $\log_{10}\left(\frac{n}{n_o} - \frac{n_p}{n_o}\right)$ is plotted against the stress for several arbitrary choices of the constant $\frac{n_p}{n_o}$. A linear graph is obtained if the asymptote $\frac{n_p}{n_o}$ is taken to be 0.64. Reference to Figure 5 shows also that:

$$\frac{n}{n_o} - \frac{n_p}{n_o} = 0.355^{-0.138S}.$$

The effect of stress on the structure is therefore described by the equation:

$$n = n_p(1 + \tau_o e^{-KS}) \tag{3}$$

where $K = 0.0138$ in this case.

It is now easy to calculate the amount of temporary structure in the unstressed vulcanizate. We have:

$$\frac{n_p}{n_o}\tau_o = 0.355 \text{ and } \frac{n_p}{n_o} = 0.64; \text{ hence } \tau_o = 0.56$$

contacts per chain which means that the temporary structure averages 1.56 particles per chain before stress is applied.

EFFECT OF HEATING ON THE STIFFNESS AND RESISTIVITY OF PRESTRESSED VULCANIZATES

The decrease in resistivity of prestressed rubber-black compounds on heating is well established[5]. In the present study the Statex-K (50 parts) vulcanizate was heated for 15 minutes at temperatures of 40, 60, 80, and 100° C, successively, and stiffness determinations (which involve restressing) were made after each period of heating. Further heating was carried out for periods of 1, 2, 4 and 16 hours, at 100° C, stiffness determinations being made as before. Figure 6 shows that some recovery of stiffness takes place as a result of heating

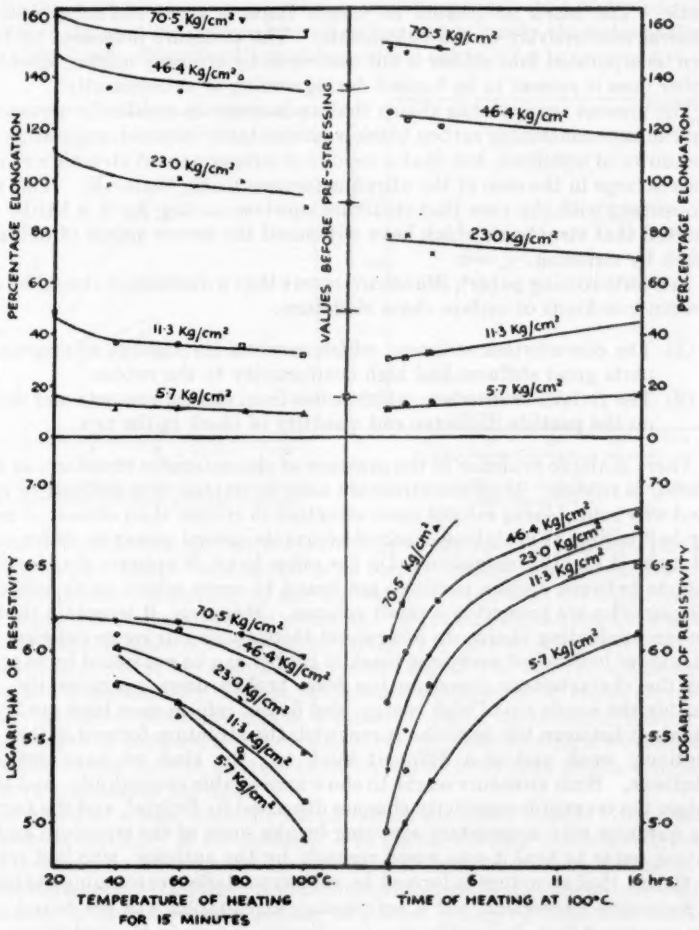

FIG. 6.—Effect of successive heating and stressing on stiffness and resistivity.

if measurements are made at stresses of the order of 20 kg. per sq.cm. or above, and for all stresses if heating is not too prolonged. The specific resistance which was measured before each determination of stiffness, decreases at first, but after one hour's heating at 100° C, it increases enormously. It should be remembered that the increases in specific resistance in Figure 6 do not indicate a simple change with time of heating, but an increasing failure of the heating to reverse the effect of the stressing which accompanied the stiffness determination.

DISCUSSION

Among the carbon blacks that exhibit chainlike groupings in air and in rubber Shawinigan acetylene black is an outstanding example. The work of Dobbin and Rossman[6] indicates that the structure of this black can be destroyed by mechanical treatment before mixing, provided such treatment is sufficiently drastic. The black so treated no longer imparts great stiffening and high electrical conductivity to the vulcanizate. The structure possessed by blacks when incorporated into rubber is not destroyed by ordinary milling operations; neither does it appear to be formed during mixing or subsequently[3].

The present research has shown that an increase in resistivity occurs when a vulcanizate containing carbon black is momentarily stressed, suggesting some breakdown of structure, but that a residue of subpermanent structure remains, which is large in the case of the ultrafine furnace black, Statex-K. This result is consistent with the view that structure survives mixing, for it is hardly to be expected that structures which have withstood the severe action of milling are broken by stressing.

In a forthcoming paper[4], Blanchard shows that a distinction should be made between two kinds of carbon chain structure:

(1) The *characteristic structure*, which survives throughout mixing and imparts great stiffness and high conductivity to the rubber.
(2) The *fortuitous structure*, which arises from chance contacts and depends on the particle diameter and quantity of black in the mix.

There is ample evidence of the presence of characteristic structure, as above defined, in rubber. If all the structure were fortuitous, it is difficult to understand why some blacks exhibit more structure in rubber than others, or explain why ball milling of acetylene black[6] destroys its special power to stiffen rubber and make it highly conductive. On the other hand, it appears that fortuitous contacts between carbon particles are found to occur where many millions of such particles are present in a small volume. Moreover, it is certain that continuous conducting chains do not persist throughout mixing as entities. The behavior of ball-milled acetylene black in rubber can be explained by supposing that the characteristic structure has been broken down permanently. Presumably the bonds are of high energy, and do not reform once they are broken. If contact between the particles is renewed, the structure formed is then comparatively weak and of a different kind, *i.e.*, the kind we have defined as fortuitous. Such structure ought to show appreciable reversibility, and should explain the reversible resistivity changes discussed by Bulgin[7], and the authors[3]. The question why momentary stressing breaks some of the structure and why heating tends to heal it was posed recently by the authors[3], who had rejected the theory that structure is formed by carbon particles rearranging themselves by Brownian movement, but a satisfactory explanation was not found. It is now suggested that during the stressing breaks appear in the fortuitous struc-

ture, and after retraction a proportion of the contacts remain broken because rubber molecules have become lodged in the gaps between the particles. Such breaks become healed if, as a result of thermal agitation, the entrapped portions of the molecules slide from between the carbon particles. Beebe, Polley, Smith, and Wendell[8] argue that there should not be "any serious barrier to the migration of a CH_2 group over the surface of a carbon particle", and hence that Brownian movement of the particles is possible. The authors think it is more feasible to invoke movement of the rubber molecules from between adjacent particles so that full contact is established. On this view, van der Waals attachments between particles must be assumed; otherwise contacts would be broken by rubber molecules moving in between particles, and heating would not be expected to increase structure.

The terms fortuitous and characteristic, as applied to structure, are not synonymous with temporary and subpermanent, respectively. Subpermanent structure is the part not affected by stressing, and is partly characteristic and partly fortuitous. Blanchard's work[4] enables a calculation to be made of the

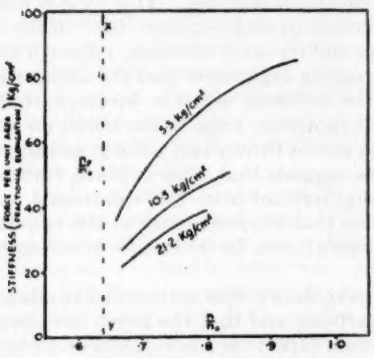

FIG. 7.—Comparison of stiffness at three stresses with carbon chain structure after prestressing.

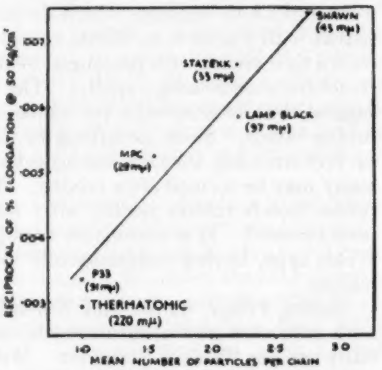

FIG. 8.—Dependence of stiffness on characteristic chain structure n_c.

characteristic structure, and for Statex-K this works out to an average value of 2.2 particles per chain. It is shown in an earlier passage that a component of the total structure amounting to approximately 1.6 particles per chain (about 36 per cent) can be destroyed by stressing. If it is assumed that none of the characteristic structure is destroyed by stress, it is easy to show that the total structure before the stress is applied is greater than 2.2×1.6, *i.e.*, 3.5 particles per chain. Unfortunately it is not yet possible to calculate this total structure with any degree of certainty, but is is probably made up of chains having an average length of between 5 and 10 particles. It should be remembered that these mean values include discrete particles; some fortuitous chains consist of very large numbers of particles.

The question arises, does the carbon chain structure broken by stressing contribute appreciably to the stiffness? In Figure 7, which combines Figures 1 and 4, the stiffness, as measured by the ratio of stress to fractional elongation, is plotted against the fraction of chain structure present after various prestresses. The change in stiffness corresponding to a fixed change in structure becomes much increased as the structure decreases, *i.e.*, as the prestress increases. It

follows that the softening can be attributed only to breakage of carbon chain structure on the assumption that the sensitivity of stiffness to structural changes increases rapidly as the structure decreases.

The calculation of structural changes from electrical resistivity is based on unpublished work[4], in which the characteristic structures of several carbon blacks are estimated on the electrical resistivity of vulcanizates. In Figure 8 the reciprocal of the percentage elongation at 50 kg. per sq. cm., which is proportional to the stiffness, is related to these estimates of characteristic structure of several blacks, for vulcanizates containing 45 parts by weight of black. There is no evidence for an increase of the change in stiffness with structure as the structure decreases, and although the graph does not exclude the possibility of a slight trend of this kind, it does indicate that it is very small if present. There is appreciable scattering of the points, but this is not surprising in view of the range of particle diameters from 28 mμ (MPC) to 270 mμ(Thermatomic).

Since the change of stiffness with structure does not increase appreciably as the structure decreases, the softening due to stress cannot be explained by breakage of structure. This seems to confirm that the stress breaks relatively weak fortuitous contacts which do not affect the stiffness. This view is consistent with Figure 6, in which, except perhaps at small stresses, the stiffness is shown to increase with prolonged heating and repeated stressing, although the structure is decreasing rapidly. The foregoing arguments lead the authors to suggest that substantially the whole of the softening is due to broken carbon-rubber bonds. Since, according to this hypothesis, some of the bonds do not survive stressing, they are not expected to persist throughout milling, and hence many may be formed after mixing. This suggests that, after rupture, carbon-rubber bonds reform readily after mixing, but not after the vulcanizate has been stressed. It is reasonable to suppose that physical bonds of the van der Waals type, having comparatively low energy, can be broken by stressing or milling.

Beebe, Polley, Smith, and Wendell[8] have shown that carbon blacks adsorb both saturated and unsaturated hydrocarbons, and that the forces are essentially van der Waals in character. We would expect the contribution of rubber-carbon bonds to the stiffness to depend on the stress and the number of bonds; the margin by which they have escaped rupture is immaterial. The data of Mullins show that at stresses giving elongation of the order of 100 to 200 per cent, the extra stiffness imparted by carbon black to rubber is almost completely destroyed by an additional 100 per cent prestretching, and it seems to follow, therefore, that the majority of rubber-carbon bonds may be easily broken in this way. Otherwise it is necessary to assume that stiffness at first decreases sharply with the number of broken bonds, subsequently becoming nearly independent of them through a wide range. Apart from being intrinsically unlikely, this assumption is untenable, since it cannot be reconciled with the familiar variation of stiffness with content of carbon. If these arguments are correct, a comparatively small number of strong bonds stiffen the rubber substantially at very high stresses, and these may not be the van der Waals type.

NOTE ON REËNFORCEMENT

The reënforcement of rubber by fillers is characterized by increased tensile strength, tearing, and abrasive strength, and increased stiffness. Stiffness is influenced little by particle size, but the other properties are very dependent on it. Prestressing has little, if any, influence on tensile strength, but on present

evidence abrasion resistance is reduced. (Tests on the Dunlop constant-energy abrasion machine on the vulcanizate used in the present investigation indicate a decrease of about 20 per cent after 250 per cent prestretch.) Assuming the truth of the authors' conclusion that the stiffening bonds broken by prestressing are between carbon and rubber, the (carbon-rubber) structure must be weakened, and so is less likely to resist the impact of the abrasive substance. The majority of ruptured carbon-rubber bonds must be presumed to be relatively weak and, in fact, before the publication of Mullins' work, Parkinson had argued[9] that carbon-rubber bonds are not in general of a high order, though one of the reasons given, namely flocculation of carbon particles in unvulcanized rubber, is not now considered valid. But it was argued also that, to account for some of the phenomena of reënforcement, it seemed necessary to postulate a limited number of strong bonds (chemisorptive or even chemical attachments), and the present thesis shows that the phenomena associated with prestressing support this concept. Beebe and his coworkers[8] have not been able to detect the presence of localized cross-linkages when unsaturated hydrocarbons were used as adsorbates for carbon black, but they admit that "only a small per cent of the carbon black need thus be associated to produce a marked effect in the elastic properties of the rubber". They find difficulty, however, in understanding why the properties of rubber steadily improve as the black loading increases, if only a small fraction of the black is effective in reinforcement. But if it is assumed that such strong linkages are only possible at localized areas on the particles, it seems probable that up to optimum loading their number would be controlled by, and proportional to, the total volume of carbon in the rubber.

On the question of the part played by carbon chain structure in reënforcement the evidence is conflicting. Ultrafine furnace blacks, with more structure, and with particles rather larger than those of channel black, give equal reënforcement as judged by tread wear, and so it might be argued that the increase in particle size is compensated for by increased structure. On the other hand, acetylene black, with both smaller particles and more structure than HMF blacks, imparts less abrasion resistance to tire treads than the latter, though giving stiffer vulcanizates. Acetylene black particles apparently have a higher degree of crystallinity than other types of carbon black[10], and this may influence their reënforcing properties.

Another fact to be noted is that when the structure of channel black is broken by remilling unvulcanized stocks, following heat treatment, resistance to tread wear of the resulting vulcanizate is, if anything, slightly increased[11], although there is a small decrease in tensile strength and tear resistance.

The above facts indicate that chain structure is not necessarily important in determining reënforcing properties other than capacity to stiffen. The small differences in reinforcing value relative to particle size between ultrafurnace and channel blacks may be related to differences in the nature and activity of the particle surfaces.

SUMMARY

The stiffening action of carbon black in rubber is due to structures formed by carbon-rubber bonds and coherent chains of particles. The softening which occurs during prestressing cannot be explained by broken chain structure, and it is thought that substantially the whole of this softening is due to ruptured carbon-rubber bonds. Prestressing does not affect the characteristic chain structure of the black particles; it breaks relatively weak fortuitous chain

structures, formed by reversible van der Waals forces between particles, which contribute little to the stiffness except perhaps at small stresses. Heating tends to reform the fortuitous structure, owing to the thermal movement of the rubber molecules, which pulls them from between adjacent particles, so that full contact is established. The majority of carbon-rubber bonds are relatively weak and are readily broken by stressing. In addition to these low-order physical bonds, a comparatively few strong bonds stiffen the rubber considerably at high stresses, and are mainly responsible for increasing the tensile strength and abrasion resistance. Such high energy linkages are possible only at localized areas on the particles.

ACKNOWLEDGMENTS

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THE NATURE AND ACTIVITY OF CARBON BLACK SURFACES *

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Of the many pigments available to the rubber industry, carbon black alone has proved capable of producing the high degree of reinforcement required in the modern tire. The basis for this superiority over other pigments, as well as the differences in reinforcing ability encountered among the various types of carbon blacks, must involve the extent and nature of the carbon black surface. While this fact has been generally recognized, it has only been within the past ten years that experimental techniques have become available which make possible quantitative evaluation of these important properties. With the development of the electron microscope and various adsorption techniques, precise evaluation of the extent of pigment surface has become possible[1]. When applied to carbon blacks, these procedures reveal an extremely fine state of subdivision. Particle diameters of from 0.1 to 0.02 micron are found for those blacks most commonly employed in the rubber industry. While particle size has been found to correlate with a number of reinforcing properties[2], among them tensile strength, hardness, and hysteresis of compounded rubber stocks, it has also become evident that the behavior of carbon black cannot be described solely on this basis. For example, pH, vulcanization retardation, and "scorching" depend primarily on the chemical composition of the carbon black surface[3]. In addition, and possibly more fundamentally associated with reinforcement, is a factor which we shall refer to as the *activity* of the surface. In addition to the extensive factor of surface area, it seems plausible that an intensive factor relating to the specific surface activity must also be considered in interpreting the reinforcing ability of carbon black. For example, it is generally recognized that the modulus properties of rubber stocks loaded with carbon black do not depend primarily on particle size of the black[4]. The fact that various treatments of the carbon black surface, among them high temperature treatment, can, as shown in Table II, drastically alter the modulus and reinforcing properties of carbon black without significantly affecting the extent of surface, is indicative of an effect associated with surface activity. The concepts of "structure" and "shape factor" have been proposed[5] to interpret the varying effects on rubber modulus produced by various carbon blacks, and it may be that the origin of this structure-forming tendency lies in the specific activity of the carbon surface.

The problem involved is not unlike that encountered in evaluating the activity of catalysts. Since heat of adsorption measurements have proved fruitful in this instance[6], we have used a similar approach in studying the surface of carbon blacks. While our ultimate interest lies in the system rubber and carbon black, it has seemed advisable to initiate our studies with less complex systems which may be treated with a high degree of precision. Consequently,

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the present paper describes measurements of the strength of binding of nitrogen and a series of C_4 hydrocarbons to the surface of a number of carbon blacks of varying reinforcing ability. Further work is in progress in which hydrocarbons of increasing complexity are being used as adsorbates.

The differential heats of adsorption of the various gases on carbon black were determined with an adiabatic calorimeter of the type previously described by Beebe[7]. The adsorption apparatus was of the type commonly employed in determining the surface area of solids by the Brunauer, Emmett, and Teller method[8]; the adiabatic calorimeter replacing the conventional adsorption cell. The calorimeter was immersed in a large Dewar flask filled with either liquid nitrogen or ice, making possible measurements at −195° or 0° C, as required. Since the Brunauer, Emmett, and Teller theory[9] yields the volume, Vm, of adsorbate required to fill the monolayer on the various samples of carbon black, the above apparatus makes possible precise measurement of the heat evolved with increasing surface coverage. The fraction of the surface covered is defined by V/Vm, where V is the volume of gas adsorbed at various points on the isotherm, and Vm is the volume required for a monolayer as derived from the Brunauer, Emmett, and Teller theory. The heat evolved on adsorption of each increment of adsorbate is reported in terms of the differential molal heat of adsorption. The values reported in the present paper are reproducible to ±5 per cent. The carbon blacks selected for study include a medium processing channel black, the same black freed of chemisorbed gases by heating in vacuum at 1000° C (devolatilized), and another sample of this MPC black partially graphitized (Graphon), by heating to 3000° C. A series of furnace blacks, including an SRF (Sterling-S), a fine furnace (Sterling-99), and an RF black (Vulcan) completes the series. The analytical properties and rubber data for these carbon blacks are summarized in Tables I and II.

RESULTS

The results obtained at −195° C, using nitrogen as the adsorbate on the channel black series, are summarized in Figure 1. The heat curves for the original MPC and devolatilized black are nearly identical, and are characterized by high initial heats, which decrease sharply with increasing surface coverage, and approach the heat of liquefaction of nitrogen beyond the monolayer. The facts that the binding energies do not depend on the chemical composition of the surface, and that the adsorption was readily reversible, indicate that the association is purely physical or van der Waals in nature. It is

TABLE I

ANALYTICAL PROPERTIES OF CARBON BLACKS

Type	Sample	Diameter* (Å)	Surface† area (M^2 per g.)	Diphenylguanidine adsorption (mg. per g. black)	Volatile matter (%)
MPC	Spheron-6	285	110	7.6	5.0
—	Spheron-6 (devolatilized)	285	120	1.1	<0.5
—	Graphon	300	85	0.8	<0.5
SRF	Sterling-S	600	24	1.7	0.6
FF	Sterling-99	420	75	1.4	1.0
RF	Vulcan	320	117	1.9	0.4

* Arithmetic mean from electron micrographs.
† From N_2 adsorption.

TABLE II

RUBBER PROPERTIES OF CARBON BLACKS*
(Data given for rubber of optimum cure)

Type	Sample	Tensile strength (lb. per sq. in.)	Modulus (300% elongation) (lb. per sq. in.)	Abrasion loss†
MPC	Spheron-6	4270	1380	260
—	Spheron-6 (devolatilized)	4270	1560	255
—	Graphon	3700	210	480
SRF	Sterling-S	3180	1030	491
FF	Sterling-99	3620	1010	342
FF	Sterling-105	3820	1370	281
RF	Vulcan	3510	1710	212

* Recipe: Smoked sheet, 100 parts; black, 50 parts; zinc oxide, 5 parts; sulfur, 2.8 parts; pine tar, 3 parts; stearic acid, 3 parts; Agerite Hipar, 1.0 parts; mercaptobenzothiazole, varied with type of black, 0.5 (FF), 0.9 (MPC), 0.4 (SRF).
† Abrasion loss = cc. stock abraded per revolution $\times 10^6$.

interesting to note, in view of the similar surface forces observed for the oxygen-covered and bare carbon surface, that outside of difference in rates of vulcanization, the reinforcing properties of these two blacks are quite similar. The partially graphitized sample (Graphon), however, gives a very different result. The initial sites of high adsorptive activity have been greatly reduced in intensity, and the surface appears to be more uniform. Again, it is noteworthy that, in this instance, the reinforcing properties as evidenced by modulus and abrasion resistance have been greatly reduced. The inflection observed in the heat curve at 0.4 of a monolayer is quite real and has, in fact, been reproduced by Joyner and Emmett[10] in an independent investigation, employing the method of isosteres. The inflection may possibly be ascribed to lateral interaction of adsorbed molecules, an effect which would presumably become more evident on a uniform surface following saturation of high energy sites.

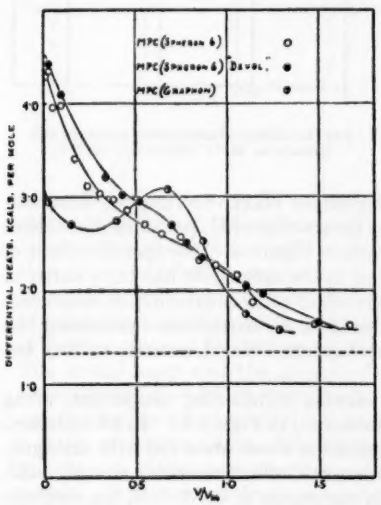

FIG. 1.—Heats of adsorption, nitrogen at −195° C.

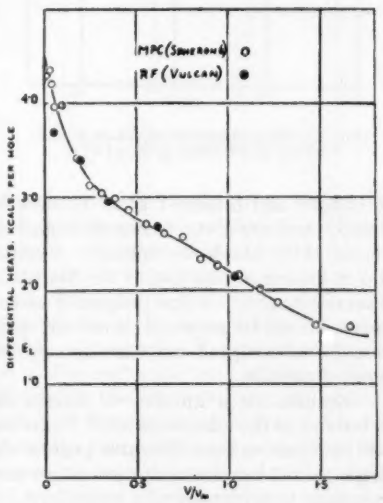

FIG. 2.—Heats of adsorption, nitrogen at −195° C.

The production of a furnace black with reinforcing properties equivalent to a fully reinforcing channel black has been an achievement of considerable interest to the rubber industry. The rubber properties of such a reinforcing furnace black (Vulcan) are reported in Table II. It is interesting to note that its surface activity as revealed by heats of adsorption of nitrogen is, as shown in Figure 2, about equal to that of an MPC black.

While nitrogen was used as the initial adsorbate to ensure evaluation of purely van der Waals forces, hydrocarbon adsorbates should prove more satisfying from the point of view of the rubber chemist. A program of study involving hydrocarbons of increasing molecular weight and complexity is in progress. At present, C_4 hydrocarbons have been most fully studied. Our first interest has been to observe whether a specific effect of unsaturation in the adsorbate could be observed. In this regard, heat of adsorption data for

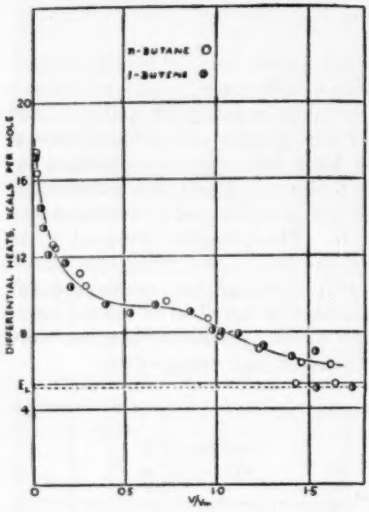

FIG. 3.—Heats of adsorption, *n*-butane and 1-butene on FF (Sterling-99) at 0° C.

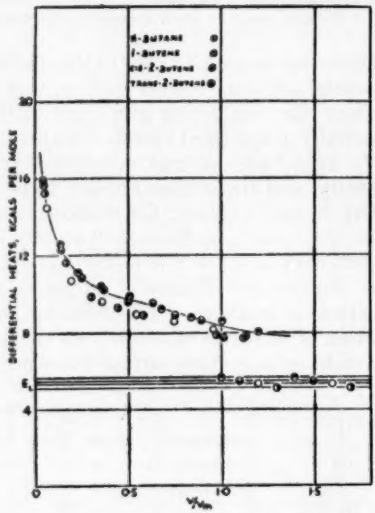

FIG. 4.—Heats of adsorption, *n*-butane and butenes on MPC (Spheron-6) at 0° C.

n-butane and butene-1 at 0° C on a fine furnace black, Sterling-99, were collected, and are given in Figure 3, and that for a series of C_4 paraffins and olefins on an MPC black are similarly summarized in Figure 4. No specific effect of the presence or position of the double bond in the adsorbate has been noted in these instances. Final judgment as to the effect of unsaturation on reinforcement should be reserved, however, until data on hydrocarbons containing the doubly interrupted unsaturation system characteristic of natural rubber become available.

Results for a number of blacks of varying reinforcing properties, using 1-butene as the adsorbate at 0° C, are summarized in Figure 5. In all instances the heat curves have the same general character as those observed with nitrogen. High initial heats of adsorption are encountered, which decrease sharply with coverage to about 0.4 of a monolayer. In the region of 0.4 to 1.0, the surfaces appear quite uniform as regards adsorptive activity, and at the monolayer the

values again decrease and approach the heat of liquefaction of the adsorbate. The high initial heats indicate sites of high adsorptive activity extending roughly over the first 40 per cent of the surface. As noted previously, partial graphitization has greatly reduced the intensity of these sites. The SRF sample shows values intermediate between the graphitized sample and the reinforcing MPC black. The fine furnace black displays a surface activity closely similar to that of the fully reinforcing MPC black. For these last two blacks, the initially adsorbed C_4 molecules give heats of adsorption of some 16,000 cal. per mole, and preliminary measurements on C_5 hydrocarbons indicate values as high as 20,000 calories on these carbons. These values are considerably larger than the heats of adsorption commonly associated with physical adsorption. In the present instance, it is probably more significant to consider the value per CH_2 group. Our present data suggest an energy of binding of

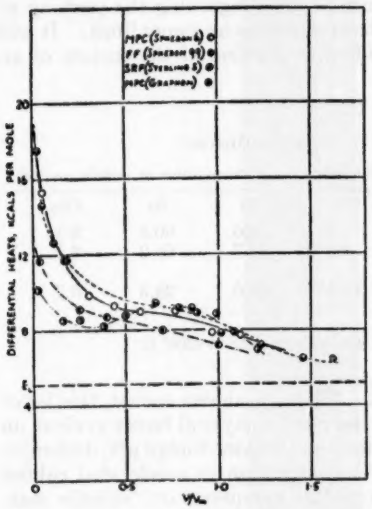

FIG. 5.—Heats of adsorption, 1-butene at 0° C.

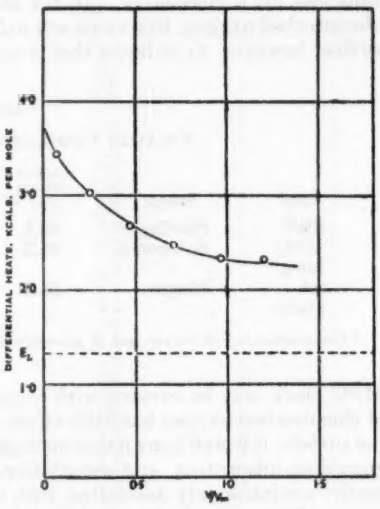

FIG. 6.—Heats of adsorption of nitrogen on MgO at −195° C.

some 4000 cal. per mole for each such group on the carbon surface. It is interesting to note that the surface activity as here measured parallels the reinforcing ability of the carbon blacks so far studied. However, it must be pointed out that this type of surface activity, characterized by the presence of sites of high adsorptive activity, is not unique to carbon black but is doubtless characteristic of most finely divided solids. Figure 6 gives heats of adsorption as a function of surface covered for nitrogen at −195° C on a sample of calcined magnesia. The initial heats and the general shape of the curve are very similar to those observed for an SRF carbon black. However, the fact remains that we have yet to observe a reinforcing carbon black with low initial surface activity. In a series of blacks those with highest activity have displayed maximum reinforcement. Obviously pigment reinforcement cannot be attributed to a single factor. It is evident from the present work that surface activity as well as particle size must be involved.

More conclusive evidence as to the nature of carbon black-rubber association may be available when experiments involving dihydromyrcene as the adsorbate are completed. It is the simplest analog of natural rubber, and adsorption on a variety of blacks at 100° C should provide data more strictly comparable to the rubber system.

Another phase of the present investigation has been concerned with the chemical composition of the surface of carbon black. As shown in Table III, the carbon content of the various grades of rubber blacks ranges from 95 to 99 per cent, the remainder consisting primarily of combined oxygen and hydrogen. The former is confined chiefly to the surface, while the latter appears to be more or less evenly distributed throughout the particle. An MPC grade of carbon black contains 3 to 4 per cent by weight of oxygen. If the packing of this chemisorbed surface oxygen is of the same order as that for physically adsorbed oxygen, then this amount of oxygen (23 cc. at STP) would be about sufficient for a monolayer. In the absence of data regarding the packing of chemisorbed oxygen, this value can only be accepted as an upper limit. It will suffice, however, to indicate that a considerable fraction of the surface of an

TABLE III

VOLATILE COMPOSITION OF CARBON BLACKS

Type	Sample	Carbon content (%)	Volatile matter (%)	Composition of volatile matter*		
				CO	H_2	CO_2
SRF	Sterling-S	99.1	<1	6.6	90.3	3.1
MPC	Spheron-6	95.2	4.6	33.7	60.2	6.1
Long ink black	Mogul	88.0	11.7	65.0	28.3	6.7

* Composition in volume-per cent of gas evolved on heating in vacuum at 1200° C.

MPC black may be covered with oxygen. While, as shown earlier, this layer of chemisorbed oxygen has little effect on the purely physical forces evident on the surface, it is well known that such phenomena as water-sludge pH, diphenylguanidine adsorption, and retardation of vulcanization in accelerated rubber stocks are intimately associated with the surface complexes or "volatile matter"[11]. The amount of such material can be determined by the loss in weight on calcining the black at 1000° C. The gases evolved under such conditions consist chiefly of CO, CO_2, and H_2, as shown in Table III. These measurements, however, tell us little of the nature of the surface complexes as they exist on the black surface. It has been suggested that they are of varying nature and complexity[12]. However, conclusive evidence has been lacking. In this laboratory we have investigated a procedure developed by Norman and Johnson[13], which appears capable of precisely defining the nature of the surface complexes on carbon black[14]. This involves identification by emission spectra of the groups or free radicals released from the carbon surface by electron excitation. This procedure involves a quartz discharge tube fitted with two cup shaped stainless steel electrodes, into which the carbon black samples are placed. The system is thoroughly evacuated, and a potential of 5000 volts is applied across the electrodes. The groups released from the surface by the impact of fast electrons or ionized molecules are excited to a higher electronic state, thus producing a characteristic discharge in the tube, which is resolved and photographed with a grating spectrograph. A jump-plate technique is employed,

FIG. 7.—Portion of a typical emission spectrum obtained from groups desorbed from the surface of a fine furnace black (Sterling 105). Five exposures obtained at 10-second intervals are shown.

TABLE IV

ANALYTICAL PROPERTIES OF CARBON BLACKS

Type	Sample	Surface area* (M^2 per g.)	Volatile matter (%)	Diphenyl-guanidine adsorption (mg. ads. per g.)	pH
FF	Sterling-105	90	0.7	1.3	9.0
MPC	Spheron-6	110	5.0	7.6	4.0
Long ink black	Mogul	400	12.0	40.0	2.8

* From nitrogen adsorption.

which makes possible an exposure every 10 seconds, which is continued until the black is completely devolatilized. A portion of a typical spectrum with the various band heads identified is reproduced in Figure 7. The observed bands are identified from data compiled chiefly by Pearse and Gaydon[15].

The surface complexes on three widely different types of carbon black have been studied. The first was an MPC rubber black, whose properties have already been discussed in the first section of this paper. The Mogul black, a "long ink" black used in the preparation of lithographic inks, is prepared by air oxidation of an MPC grade of black. Sterling-105 is a typical fine furnace black. Pertinent analytical data on these three blacks are presented in Table IV. The various groups released from the surface of each sample, as identified by their emission spectra, are presented in Table V. The figures given represent the observed intensities of the emission. Since the brightness of the emission is not the same for all radicals, it is not permissible to estimate the relative concentration of one radical with respect to the other. It is permissible, however, to compare the relative intensity of the same group in the various carbon samples, since the overall intensity must be indicative of the concentration of excited groups. The data substantiate the conclusion that there is a variety of chemical complexes on carbon black surfaces. CH and CH^1 are both measures of carbon to hydrogen linkages, but the latter arises from a much higher excitation level than the first, indicating that hydrogen is bound to carbon in at least two configurations. Chemically combined nitrogen in quite low concentration is indicated by $-NH$, N_2^+, and the cyanogen radical $-CN$. A considerable volume of oxygen is present as $-OH$. The observed intensities of $-CHO$ and CO_2^+ indicate a high concentration of these radicals in the discharge. The CHO radical must have been associated with the carbon surface as an aldehyde group. The reported intensities of this radical are of the same order as those observed in alpha-cellulose. CO_2^+ is always identified in the spectrum of organic acids, and it is safe to conclude that it arises from carboxyl groups attached to the carbon black surface. The increasing concentrations of CHO and CO_2^+, as listed in Table V, are to be anticipated in view of the

TABLE V

EMISSION SPECTRA INTENSITIES OF GROUPS DESORBED FROM CARBON BLACK SURFACES

Type	Sample	CH	CH^1	C_2	CO	CO^+	CO_2^+	OH	N_2^+	NH	CN	CS	CHO
FF	Sterling-105	7	23	13	13	—	1	36	18	56	30	4	4
MPC	Spheron-6	12	28	16	38	—	8	84	4	74	44	7	12
Long ink black	Mogul	24	42	28	36	2	11	64	2	54	36	4	16

method of preparation of the blacks. The fine furnace black, Sterling-105, does not encounter a strongly oxidizing atmosphere until it has cooled to temperatures too low (40° C) to make possible significant chemisorption of oxygen. The MPC black is prepared by impingement and has ample opportunity, during, or just before deposition, to chemisorb oxygen from the surrounding air. The long-ink black, Mogul, as already pointed out, is prepared by additional air aftertreatment of an MPC black at elevated temperatures.

The increasing concentrations of CO_2^+ encountered in this series of blacks, presumably arising from surface carboxyl groups, may account for the increasing acidity of the blacks as indicated by their pH values. The magnitude of the pH of a given sample is doubtless also influenced by the OH groups present in considerable concentration on the surface. However, a more precise interpretation of these data must await calibration of the method to provide information as to the relative concentration of each type of complex and its concentration per unit of surface.

Further conjecture at this stage may be premature. We feel, however, that the work so far completed demonstrates differences both in the specific activity and chemical composition of carbon black surfaces. It is hoped that further work employing the methods described will reveal the nature of the association between rubber and carbon black as well as the possible reactions which may occur on the surface of this versatile pigment.

SUMMARY

While the electron microscope and adsorption isotherm techniques for evaluating the particle size and surface area of carbon blacks have been particularly valuable in interpreting their behavior in rubber, they also emphasize the fact that reinforcement cannot be interpreted solely on this basis. The activity or nature of the surface must also be considered.

Heats of adsorption offer a means of evaluating surface activity. The differential heats of adsorption have been measured by precision calorimetry for nitrogen and a series of C_4 hydrocarbons on a group of carbon blacks of varying reinforcing ability. Initial sites of high activity were detected. Surface activity decreases with increasing surface coverage. The magnitude of the initial heats parallels the reinforcing properties of the blacks studied. The surface activity and reinforcing ability of an MPC black was found to be greatly reduced by high temperature treatment. These effects were not influenced by the chemical nature of the surface, *i.e.*, the presence of chemisorbed oxygen or volatile substances.

In a further phase of this study, the nature of the surface oxide complexes present on carbon blacks has been studied by means of their emission band spectra in a special vacuum discharge tube. Aldehyde and carboxyl radicals were observed in high concentration. Hydroxyl radicals were also present in nearly equal concentration. These data offer a satisfactory interpretation of the pH properties of carbon black and also should prove of value in interpreting other chemical properties.

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THEORY OF FILLER REËNFORCEMENT. II *

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Finely divided powders and particularly carbon blacks enhance, in general, the desirable physical properties of rubber. The nature and magnitude of this enhancement depend on the physical properties of both the filler and of the rubber matrix. The enchanced physical properties of the rubber-filler system can be conveniently divided into two types. The properties of the first type depend mainly on the particle shape and the concentration, and they are independent of the size and surface characteristics of the filler. Such properties are the stiffening of the stress-strain curve, the increase in dielectric constant, and loss. We shall call such properties of the *modulus type*. The properties of the second type depend sensitively on size and sometimes on surface characteristics, in addition to a general dependence on concentration and, possibly, to a lesser extent on shape. Such properties are tensile strength and tear resistance. Wear resistance and abrasion resistance depend also sensitively on both size and shape. All these properties we shall call of *tensile type*. Their dependence on concentration is represented by a curve concave to the concentration axis and passing through a maximum; for modulus-type properties, the analogous curve is convex, at least in the commercial loading range.

A theory of the properties of the modulus type was given by the author several years ago[1]. The present paper is a further elaboration of the theory, including new experimental material to test it and a summary of contributions of other authors to the subject.

The theoretical treatment of the modulus type properties is based on the fact that the elastic dielectric behavior of the rubber (before incorporation of the filler) may be described by the theory of elasticity, the theory of dielectrics, and characterized by certain constants, like Young's modulus or dielectric constant. The enhancement of the elastic and dielectric behavior is then explained by a change of these constants without altering the theory which described the behavior of the gum stocks.

Unfortunately, no quantitative theory yet exists which can explain properties of the tensile type for the gum stock. Therefore attempts to explain the enhancement of tensile strength by fillers are necessarily restricted to a more or less qualitative correlation of tensile strength with properties of the filler and of the rubber.

GENERAL TREATMENT OF MODULUS TYPE PROPERTIES

Generalizing somewhat the earlier treatment[1] we define a physical property p^* of the rubber plus filler (briefly: tread stock) as belonging to the modulus type if the relative property: $p_r = p^*/p$, depends only on the shape and volume concentration of the filler.

$$p_r = p^*/p = p_r(f,c) \tag{1}$$

* Reprinted from the *Proceedings of the Second Rubber Technology Conference*, London, 1948, pages 353–362.

Here f is a shape or form factor (equal to unity for spheres), c is the volume concentration, *i.e.*, the volume of the filler particles divided by the total volume of rubber and filler; p is the corresponding property of the rubber matrix, which may not always be approximated by the corresponding property p_o of the gum stock. We shall return to this point a little later. According to our definition, p_r is a universal function of f and c; it should not depend on (1) temperature, (2) particle size, (3) specific particle-rubber interaction, *e.g.*, different type fillers in the same rubber and the same filler in different type rubbers should yield the same p_r. These negative characteristics of p^* can be all checked experimentally and, if found valid, establish p^* as a property of modulus type.

A somewhat specialized form of Equation (1) is obtained if we assume that, for small concentrations, p_r may be developed into a series according to integral powers of c with coefficients depending upon particle shape:

$$\frac{p^*}{p} = p_r = 1 + \alpha_1 c + \alpha_2 c^2 + \ldots \tag{2}$$

For elongated particles, one can set, introducing a form factor, f:

$$\alpha_1 = \beta_1 \cdot f;\ \alpha_2 = \beta_2 \cdot f^2 \qquad (\beta_1\beta_2 \text{ pure numbers of order 1}) \tag{3}$$

Another factor, γ, may be introduced to describe agglomeration by the particles ($\gamma = 1$, *i.e.*, no agglomeration):

$$\alpha_1 = \beta_1 \cdot \gamma \cdot f \tag{4}$$

The values of β_1 and β_2 are given later in the text.

We have to distinguish between the actual and the calculated concentration. The former may differ from the latter because of solvation, *i.e.*, strong binding (adsorption) of rubber molecules to the filler particles.

As pointed out in our previous paper, a knowledge of the coefficients α_1, and α_2 alone makes possible a simple determination of solvation by determining:

$$\lim_{c\to 0} \frac{p_{sp}}{c} = \lim_{c\to 0} \frac{p^*}{p} - 1$$

$\frac{p_{sp}}{c}$ may be called reduced p and the above limit of the reduced p may be called the intrinsic p introduced by Kraemer for the special case of viscosity and designated by $[p]$. Instead of the reduced p one may also use $\frac{lnp_r}{c}$:

$$\mu\alpha_1 = [p] = \lim_{c\to 0} \frac{lnp_r}{c} = \lim_{c\to 0} \frac{p_{sp}}{c}; \tag{5}$$

μ gives then the amount of solvation.

INTERACTION BETWEEN FILLER AND RUBBER AND BETWEEN THE FILLER PARTICLES

In our previous paper we have effectively assumed that the forces between rubber and the filler particles are of the same order of magnitude or even stronger than the cohesive, *e.g.*, van der Waals, forces in rubber. This means wetting of the filler particles by rubber. Then we have for spherical nonagglomerating filler particles:

$$\alpha_1 = 2.5;\ \alpha_2 = 14.1$$

for both viscosity (η^*) and Young's modulus (E^*).

This wetting is nonspecific, implying van der Waals type forces between rubber and filler. Even if rubber is stretched, the adhesion of rubber to the surface of the filler particles persists. However, the rubber molecules have considerable mobility on the surface of the filler. This means that the filler particles themselves have a considerable mobility in the rubber matrix.

Assumption of wetting is one limiting case. Another possible limiting case is the assumption of nonwetting. Then the forces between rubber and the filler particles are very much smaller than the cohesive forces in rubber. Under this assumption we have smaller coefficients $\alpha_1, \alpha_2, \ldots$ in Equation (2) than for the case of wetting.

There is possibly a third type of strongly wetting fillers. The rubber molecules adhere then to the surface of the fillers by localized and specific chemical bonds. Unlike the case of nonspecific interaction, such an interaction cannot be treated by a quantitative macroscopic approach. Qualitatively, however, one would expect a relation of the form of Equation (2) still to hold, but with $\alpha_1, \alpha_2, \ldots$ dependent on temperature and on the particular rubber-filler combination. In general, one would expect that $\alpha_1, \alpha_1, \ldots$ would be larger than for the case of wetting.

That carbon blacks wet rubber and have the expected high mobility in the rubber matrix is indicated by the studies on electrical conductivity of carbon black loaded stocks[2]. There is a marked increase in the conductivity of annealed stocks (relaxing of internal strains) and a decrease of the conductivity on stretching and subsequent increase when a stretched sample is relaxing its stress. This behavior is in keeping with recent studies on the adsorption of gases by carbon black[3].

Filler-filler interaction may lead to the formation of chain structures. The correlation of chain structures (as observed directly in electron micrographs and indicated by the behavior of conducting blacks) and the fast increase in modulus with the concentration of such structural blacks may be explained by the dependence of the coefficients $\alpha_1, \alpha_2, \ldots$ on a shape factor, *i.e.*, as a filler particle we take a whole chain. This explains the behavior of high-modulus blacks.

VISCOSITY OF TREAD MIXES

An approximate measure of the stiffening action of carbon black is the socalled Mooney viscosity of the mix: rubber and black. It is only an approximate measure, because the flow of the mix in this viscometer is probably not Newtonian.

The theoretical equation for the relative viscosity is of the form of the Equation (2) with $\alpha_1 = 2.5$ and $\alpha_2 = 14.1$:

$$\eta_r = \frac{\eta^*}{\eta} = 1 + 2.5c + 14.1c^2 + \ldots \qquad (6)$$

The first term is the well known Einstein term, while the second term is that obtained by Guth and Gold[4] on computing the hydrodynamic interaction of pairs of particles.

Observations of Vand[5] on glass spheres suspended in a liquid show accurate validity of the theoretical Equation (6) up to 20 per cent and still fair agreement at 25 per cent concentration (cf. Figure 1). Smith[6] has shown the validity of Equation (6) in the same concentration range for rubber latex. This encourages the application of Equation (6) right up to commercial loadings (about 25 per cent on volume).

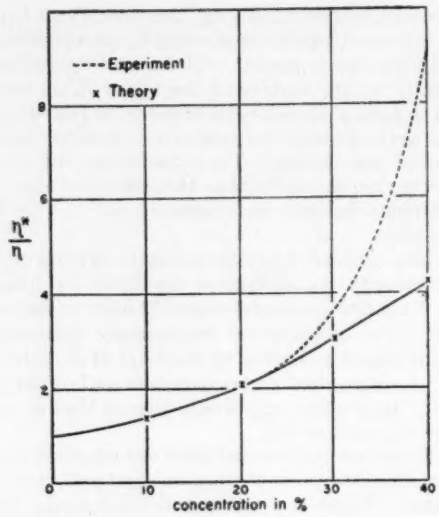

FIG. 1.—Viscosity of glass spheres suspended in a liquid. Crosses represent the theoretical Equation (6). The dotted curve represents the experimental data of Vand.

The relative Mooney viscosity of an unvulcanized mix of GR-S and carbon black (Continental A devolatilized), taken after a 4-minute run at 212° F, is plotted and compared with Equation (6) in Figure 2. Approximate agreement is seen, though some experimental points lie below the theoretical curve. For other blacks in the same GR-S mix, the relative Mooney is still lower. The flow in a Mooney viscometer is probably not Newtonian. In addition, it is possible that the degree of wetting of a carbon black in rubber increases during vulcanization.

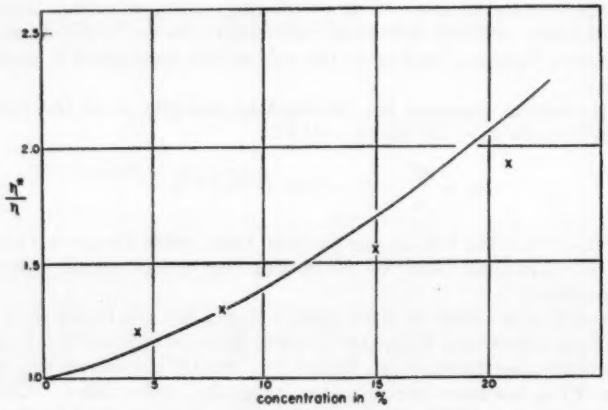

FIG. 2.—Relative Mooney viscosity of an unvulcanized GR-S–carbon black mix. Curve: Equation (6); crosses: experiment.

The reduced Mooney viscosity is at the highest concentration used in this work (c = 20.84 per cent), the smallest for P-33 (1.06) and increases for the other blacks: SRF (1.19), lamp (1.35), A (1.78), and finally comes close to the theoretical value of 2.13 for A devolatilized (1.92). We bring these data and also Figure 2 only to signalize a trend rather than attempt a quantitative comparison with theory.

STRESS–STRAIN PROPERTIES OF TREAD STOCKS

Stress-strain curves were taken with a fast stress-strain apparatus[7] with which it was possible to stretch rubber to 200 per cent extension in 1 second.

The reduced Young's moduli for first extension and equilibrium (stretching repeated 5–10 times to obtain minimum hysteresis loops) are plotted in Figures

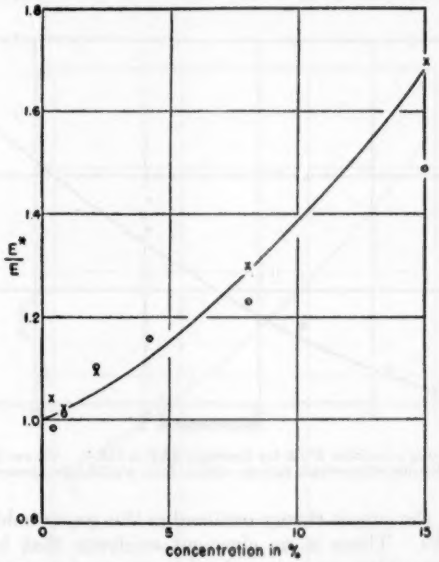

FIG. 3.—Relative Young's modulus E^*/E for P-33 in GR-S. Curve: Equation (6); crosses: from first extension stress-strain curves; circles: from equilibrium stress-strain curves.

3, 4, and 5 for P-33, Continex SRF, and Witco lampblack. Reasonable agreement with the theoretical equation of our previous paper:

$$\frac{E^*}{E} = 1 + 2.5c + 14.1c^2 \tag{7}$$

was obtained for P-33 black[8], while the values for SRF and lampblack lie higher than the theoretical curve. This was to be expected from the chain structure of SRF and of lampblack. A better agreement could be obtained using the relation:

$$\frac{E^*}{E} = 1 + 0.67fc + 1.62f^2c^2 \tag{8}$$

also given in our previous paper. This holds *a fortiori* for the channel blacks, Continental-A and Continental-A devolatilized.

Variability within samples and in each sample prevented a determination of solvation using Equation (5) and of the factor λ using Equation (3).

It is hoped that both these problems can be investigated again by more careful compounding technique. The fault was certainly not with the stress-strain apparatus, which showed a stiffening of the stress-strain curve by only 0.44 per cent carbon black.

In the present study, all loaded stocks and the gum stock were compared for the same vulcanizing period (45 minutes) chosen as closest to maximum tensile strength for the majority of the studies. It is well known that blacks retard vulcanization, and it is possible that corresponding increases in modulus are counterbalanced by such a retardation. However, such an effect could play a role only at higher (15 to 25 per cent) concentrations.

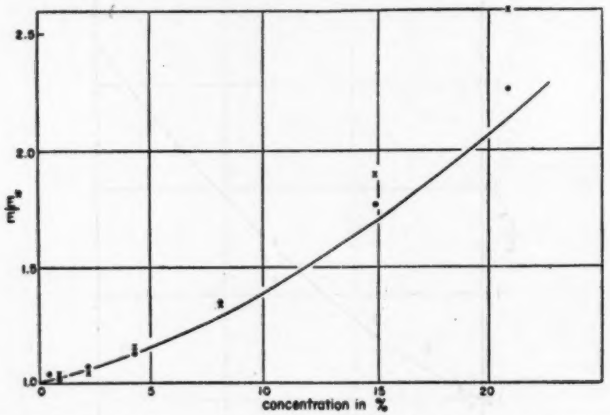

FIG. 4.—Relative Young's modulus E^*/E for Continex SRF in GR-S. Curve: Equation (6); crosses: from first extension stress-strain curves; circles: from equilibrium stress-strain curves.

Summarizing, the simple theory outlined in this paper holds reasonably well for wetting blacks. There is no clear-cut evidence that highly reinforcing channel blacks wet rubber more strongly than assumed in our theory. Cases of fillers which do not wet well are known. The action of high modulus blacks can be reasonably well explained by assuming a chain structure which is not entirely *ad hoc*, and is observable by the electron microscope. More accurate compounding techniques and great care in the choice of equivalent vulcanizations will be necessary to check possible solvation and stiffening of the rubber matrix, compared with the gum stock.

Rehner[9] was the first author to apply the theory of elasticity to discuss the stresses around filler particles. Then the author presented his previous paper[10] in which Equations (2), (6), (7), and (8) of the present paper were first given. Experimental evidence was presented also showing that Equation (6) represents fairly well the dependence of the relative modulus upon concentration. Independently, and about the same time, Smallwood[10] arrived at the Equation (6), but without the quadratic term; he presented also experimental material showing that various fillers, among them P-33, fit the straight line $E^* = E(1 + 2.5c)$,

while channel black gives higher values. Goldfinger[11] subsequently pointed out that Smallwood's data agreed on the whole better with our Equation (6), including the quadratic term. Smallwood used equilibrium stress-strain curves, and his data for P-33, for instance, show the same trend as our data.

Goldfinger[11] presented evidence for a preferential adsorption of shorter GR-S chain molecules on carbon black. The remaining longer chains lead, then, to a stiffening of the matrix between the filler particles when compared to the stiffness of the gum stock. Such effects should show up in solvation and in a value $\lambda > 1$ of the relative modulus of the tread stock when extrapolated to zero concentration. As pointed out earlier in this section, such effects could not be detected in the present work, probably because they were masked by other effects and by variability between different test sheets and within the same test sheet. No doubt, however, preferential adsorption of rubber components on the black is an important factor in understanding the action of fillers in rubber.

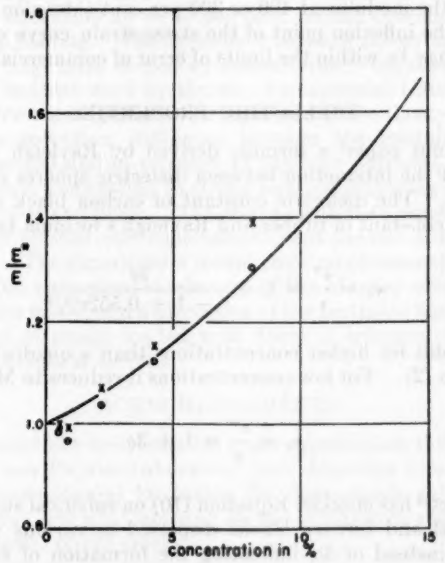

FIG. 5.—Relative Young's modulus E^*/E for Witco lampblack in GR-S. Curve: Equation (6); crosses: from first extension stress-strain curves; circles: from equilibrium stress-strain curves. E^*/E values lower than one are due to variability between test samples.

Recently Cohan[12] presented extensive material to check the predictions of our theory. He showed that the modulus of a set of channel blacks at 400 per cent extension is for smoked sheet, GR-S, GR-I, and GR-M, independent of particle size, except for the smallest blacks used (R-40; 10 mμ) which impart a slow rate of vulcanization. All stocks were vulcanized to their maximum tensile strengths. Cohan found also an increase of the Williams plasticity, *i.e.*, decrease of plasticity, with particle size. For Continex HMF in TR-S and in smoked sheet, he found that the dependency of the modulus on concentration may be represented by our Equation (6), with a shape factor $f = 6$ up to 28.5

per cent concentration. At higher concentrations the experimental values are higher than the theoretical ones. This one would expect, on the basis of our Figure 2. There may be also an increase of f at higher loadings, due to interlocking of clusters, as Cohan mentions. The shape factor $f = 6$ is about that which one would obtain from electron micrographs of HMF type of blacks. Cohan emphasizes the practical significance of the agreement between the experimental values and the theoretical equations. From a known shape factor one can predict approximately the dependence of the modulus on concentration. This holds even at loadings so high that the use of the theoretical equation cannot be justified really.

For calcium carbonates in smoked sheet, GR-S, and GR-I, Cohan checked our Equation (6), both for independence of the modulus on particle size and for the dependence on concentration.

In our opinion, Cohan's interesting work indicates the same trend as our work, but the quantitative checks of our theory have to be considered with the somewhat larger margin of error involved in the use of commercial testers. Finally, taking the modulus at 400 or 300 per cent extension neglects the shift by the filler of the inflexion point of the stress-strain curve of the gum stock, but that again may be within the limits of error of commercial testers.

DIELECTRIC PROPERTIES

In our previous paper[1] a formula derived by Rayleigh was given, which takes account of the interaction between dielectric spheres embedded in a dielectric medium. The dielectric constant of carbon black is large compared to the dielectric constant of rubber and Rayleigh's formula takes on the simple form:

$$\epsilon_r = \frac{\epsilon^*}{\epsilon} = 1 - \frac{3c}{c - 1 + 0.552c^{10/3}} \tag{9}$$

This formula holds for higher concentrations than a quadratic formula of the type of Equation (2). For low concentrations it reduces to Maxwell's formula:

$$\epsilon_r = \frac{\epsilon^*}{\epsilon} = 1 + 3c \tag{10}$$

Recently Voet[13] has checked Equation (10) on spherical suspensions. However, for channel and furnace blacks dispersed in various vehicles he found values of $11.6c$ instead of $3c$, indicating the formation of elongated clusters. It will be interesting to see whether the viscosity of these suspensions indicate the same behavior. Experiments are under way in our laboratory.

APPENDIX

Formula for stocks used in experimental work:

	Weight
GR-S	100
Mercaptobenzothiazole	1.5
Zinc oxide	5
Witco No. 20 softener	5
Sulfur	2
Carbon black	from 0.5 to 30

Vulcanized 45 minutes at 307° F

SUMMARY

Modulus-type properties of loaded rubber depend mainly on the shape and the concentration of the filler particles and are almost independent of the size and the surface characteristics of the filler. The author's theory of these properties is patterned after the theory of viscosity of suspensions, and implies nonspecific wetting between rubber and filler particles, making possible considerable mobility of the filler particles in the rubber. Such mobility is in agreement with studies of the electrical conductivity of carbon black loaded stocks and of the adsorption of gases by carbon blacks. Fillers with spherical particle shape like calcium carbonate and P-33 (which do not form chainlike structures) obey the theoretical equations for spherical particles. Fillers like high modulus and channel carbon blacks whose primary spherical particles agglomerate into chainlike secondary particles obey theoretical equations for the secondary particles characterized by a shape factor. The assumed chain formation and the values for the shape factors are in approximate agreement with conclusions from electron micrographs. Experimental arguments are given for the validity of the theoretical equations up to 25 per cent volume concentration, which is the usual technical loading. The agreement between theory and experiment is within the rather large error caused by nonuniformity between and within the test samples, and in some work by the use of commercial testers, and the difficulty of comparable vulcanizations. Refinements of the theory are introduced, including possible solvation, difference between the modulus of rubber in absence ("gum" stock) and in presence of the filler particles, and various degrees of wetting from nonwetting to strong wetting (implying specific chemical bonds between rubber and filler). The above mentioned sources of error in the experimental work prevent safe conclusions about the necessity of introducing such refinements. The experiments include new measurements of stress-strain properties of loaded vulcanized stocks and of the Mooney viscosities of unvulcanized rubber-filler mixes, and a discussion of the pertinent literature. For the dielectric constant of stocks loaded with fillers of spherical primary particle shape, a simple formula is derived.

ACKNOWLEDGMENTS

The author would like to express his great appreciation to S. L. Dart of the Notre Dame Polymer Physics Laboratory (now American Viscose Corporation, Marcus Hook, Pennsylvania) for taking the stress-strain data, and to L. H. Cohan of the Witco Chemical Company for the preparation and testing (including the Mooney tests) of the stocks.

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FRESH HEVEA LATEX. A COMPLEX COLLOIDAL SYSTEM *

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INTRODUCTION

It has already been established that Hevea latex contains yellow substances which may be separated by centrifuging the latex. This is demonstrated by the yellow sludge that remains in the bowl when ammoniated latex is clarified by centrifuging in a separator. Scientific investigation of these yellow fractions is not new. Frey-Wyssling[1] found, by microscopical investigation of Hevea latex, that there were yellow globules among the pear-shape rubber particles. It has been established that these yellow globules are somewhat bigger than the rubber particles and much fewer in number. Eaton and Fullerton[2] found that the yellow color is due to carotin. Other investigators have been De Vries, Van Harpen, Altman, and Kraay.

In our own experiments we first repeated the Frey-Wyssling investigation and then centrifuged the latex in tubes in an attempt to collect the very few yellow globules. This experiment showed, however, that when ammoniated latex was centrifuged in a tube no separation of yellow particles took place. When a similar experiment was conducted by centrifuging fresh unammoniated latex, however, a yellow viscous mass was formed and this mass, which constituted a separate layer with sharp boundaries, was of a greater proportion than we had anticipated. It is known that when in a typical manufacture of sole crepe the first fraction is removed by fractional coagulation, this fraction contains 15 to 20 per cent of the total solids of the latex. Our investigations have shown that the components of this first fraction are constantly present in fresh latex as a separate phase which has different properties from the remaining part of the latex.

MICROSCOPY OF HEVEA-LATEX[3]

The microscopic picture of Hevea latex has already been described. It has been agreed that latex is a dispersion of solid particles in a liquid medium. One cc. of latex contains about 10^{13} particles varying in size from 0.2 to 1.5μ. It is not our intention to discuss here the exact shape of the rubber particles but only to stress the fact that most investigators make use of very dilute ammoniated latex to obtain distinct pictures.

Undiluted (ammoniated) latex can be examined only in very thin layers, such as are obtained by pressing a very small drop of latex between a slide and cover glass so that the surface tension of the liquid keeps the two glass surfaces pressed together. A more satisfactory method is to place a drop of latex on a small concave watch-glass and to cover it with a cover glass.

With undiluted ammoniated latex, it is possible to observe the rubber particles lying closely together in vivid Brownian movement. Observed through

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a magnification of 200 ×, it is not possible to observe the separate particles but only to see a gray background consisting of glittering elements. When the cover glass is lightly pressed, the whole mass is observed to flow.

A totally different result is obtained when undiluted fresh latex is used. The gray glittering mass is there as before, but it is interspersed with a great number of clear transparent islands, irregularly shaped and of different sizes (see Figure 2). When the cover glass is pressed the gray mass flows rapidly between the islands, these elements behaving as inert colloidal viscous masses. These islands are not solid, and when the cover glass is moved they change their shape, and the islands, which for reasons explained later we have named lutoids, are not optically empty. On closer examination they appear to contain embedded elements, mostly rubber particles. Under microscopic examination the lutoids are estimated to occupy $\frac{1}{8}$ to $\frac{1}{4}$ of the total volume of the latex.

The lutoids vary in appearance according to the period of time which elapses between tapping and microscopic examination. In freshly tapped latex the lutoids are smaller and examinations at different intervals after tapping led to the conclusion that they are formed out of small colloidal globules (which, however, are much bigger than the rubber particles), which have agglomerated and partly flowed together (Figures 1, 2, and 3). After a few hours the lutoids become more agglomerated and appear less viscous or even coagulated. This reaction is accentuated when the latex is stirred.

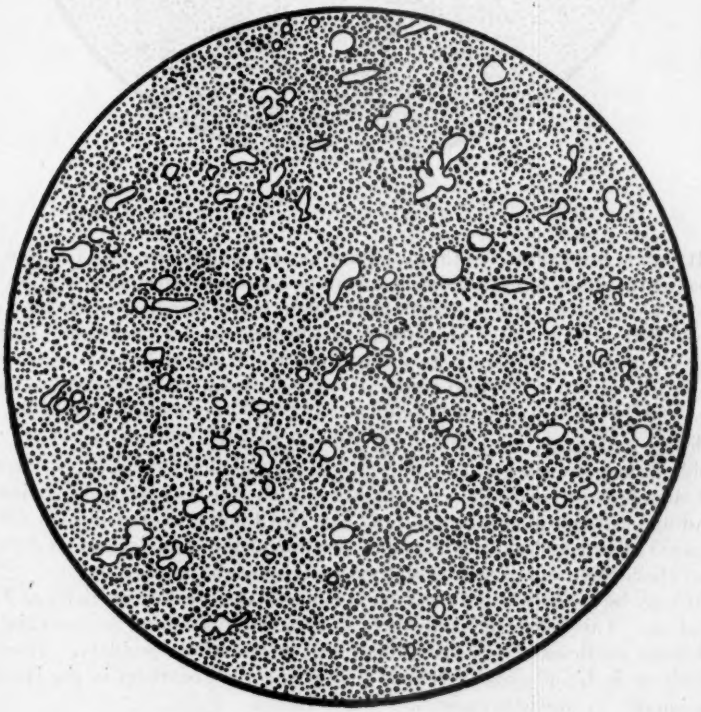

FIG. 1.—Magnification 450 ×. Hevea latex one hour after tapping.

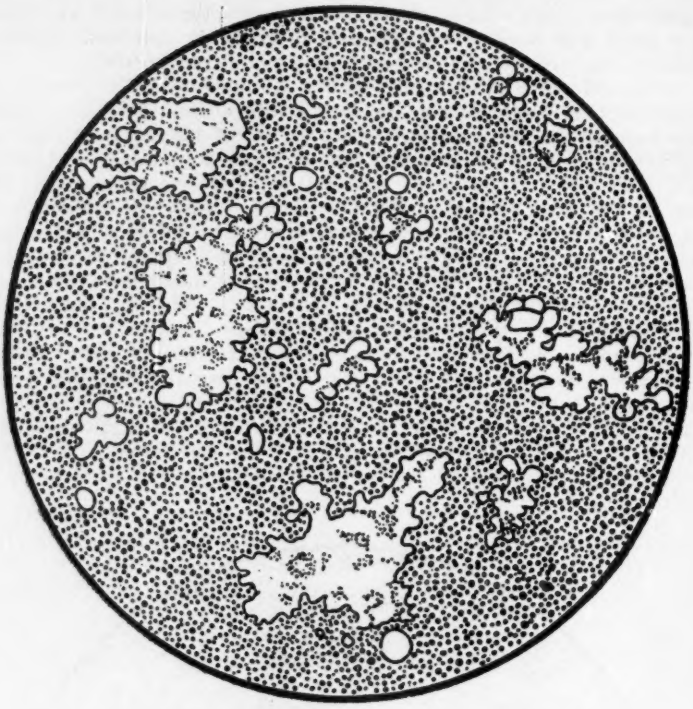

FIG. 2.—Magnification 450 ×. Hevea latex two hours after tapping.

It should be emphasized that lutoids appear to be able to exist as a separate phase in the latex serum, which is a watery solution containing proteins and salts. The phenomenon resembles those observed by Bungenberg de Jong with his socalled coacervates. An interesting phenomenon was brought about by allowing a drop of ammonia to diffuse into the latex under the cover glass, whereby it was observed that the lutoids slowly dissolved and after a time the same picture was seen as with ammoniated latex. A further experiment was made by adding pure water, which gave a totally different reaction. The lutoids shrank and coagulated and their viscous colloidal nature disappeared, so that they became rigid solid agglomerates. In a third experiment, carried out by adding salt solution, *e.g.*, 0.1 *N* KCl or NaCl solution, the lutoids neither dissolved nor coagulated. The whole question of the colloidal chemical stability of the lutoids is still under observation in our laboratories.

It may be asked why no mention is made of the socalled particles of Frey-Wyssling. This omission is purposely to avoid confusion and to stress the fact that these particles play a very minor role in the whole problem. They are difficult to find, and appear as clear yellow spherical particles in the latex or, occasionally, as particles embedded in the lutoids.

CENTRIFUGING FRESH LATEX

As already mentioned in the introduction, when fresh latex to which nothing is added is centrifuged in tubes, two separate layers of latex are formed. (This experiment was carried out with a centrifuge working at 2000 revolutions per minute for a period of 20 minutes.) The yellowish substance which separated at the bottom was equivalent to 20 to 30 per cent of the volume of the latex. The other part of the latex, which was pure white, removed above. We named these two parts, respectively, the yellow and white fractions of the latex.

When the latex is diluted with a large quantity of water or when a considerable amount of ammonia is added, *e.g.*, to above pH 9, this separation into two fractions does not occur. The addition of 10 per cent of water to latex produces a marked diminution in the quantity of the separated yellow fraction, and when 25 per cent of water is added, it becomes impossible to separate the yellow fraction by means of a centrifuge. This last fact is not quite in accord with results of McColm[4], which became known when our work on the yellow and white fractions was already in an advanced stage. McColm centrifuged fresh latex which was diluted 1:1 with distilled water and obtained a "considerable quantity of sludge". But McColm centrifuged with a Sharples supercentrifuge,

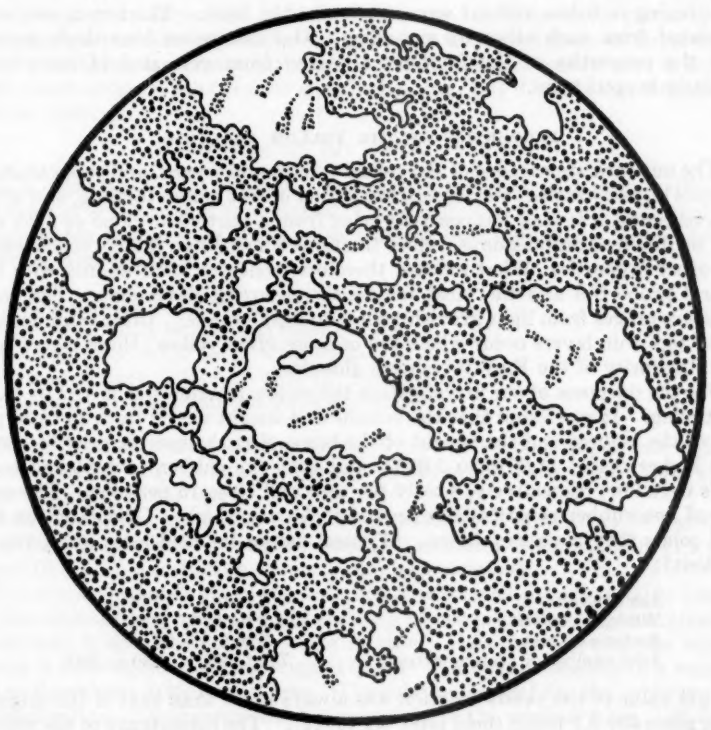

FIG. 3.—Magnification 85 ×. Hevea latex four hours after tapping.

which works at 40,000 r.p.m. We have now established that the addition of water to the latex causes the lutoids to stiffen and shrink, forming rigid agglomerates. It would appear, therefore, that these agglomerates cannot be separated with a centrifuge working at only 2000 revolutions a minute, but that with higher speeds of centrifuging they can be separated.

By far the greater part of the yellow fraction when separated from fresh undiluted and unammoniated latex consists of the lutoids, while in addition, it contains all Frey-Wyssling's yellow globules but comparatively few rubber particles. Thus the yellow fraction comprises all the nonrubber components of the latex which occur as independent substances.

The next step in our investigations was to try to separate the yellow fraction in a more technical way by centrifuging in a De Laval separator. It was found that latex to which nothing was added was often too unstable for this operation, but that this could be overcome by raising the pH slightly, *e.g.*, to about 7, thereby increasing the stability of the latex without changing the condition of the lutoids. When this was done, it became possible to separate the yellow fraction by centrifuging[5].

CHEMICAL AND PHYSICAL PROPERTIES OF THE FRACTIONS

For studying their properties, the fractions were separated by means of centrifuging in tubes without any addition to the latex. The two layers were separated from each other by siphoning. Our discussion here deals mainly with the properties of the fractions obtained from normal field latex from regularly tapped trees.

PROPERTIES OF THE YELLOW FRACTION

The outward appearance of the yellow fraction may vary, and this variation depends on the weather, the season, the period of rest before tapping, and other circumstances. It may happen that latex from a particular clone or field will give, on different tapping days, yellow fractions which differ, in color consistency, and other properties. What follows, therefore, concerns itself mainly with the general properties and the most frequently occurring deviations. The color variation ranges from light grayish yellow to dark orange. Often, and usually at the top, thin layers occur which are of more vivid yellow; these layers contain a majority of the Frey-Wyssling's globules.

For the purposes of our investigation the yellow fraction was mixed by careful stirring. It was found that the volume and weight varied from 20 to 30 per cent of the volume and the weight of the latex, that the specific gravity was a little higher than 1 (1.0016 to 1.0051) and that dry rubber content and total solids were low; respectively, 8 to 10 per cent and 13 to 15 per cent. The content of non-rubber constitutents proved to be very high. Calculated on the total solids they were as follows. (Typical values for field latex are given in brackets):

Ash content	8 to 9%	(1.6%)
Nitrogen content	2.2 to 2.7%	(0.65%)
Acetone extract	6 to 7.5%	(2.7%)
Acid number of acetone extract	750 to 900	(230 to 290)

The pH value of the yellow fraction was always lower than that of the original latex, generally 5.7 to 5.8 (field latex 6.1 to 6.3). The consistency of the yellow fraction varied from the consistency of syrup to the consistency of porridge. Generally the yellow fraction was very unstable, and directly after separation it

became more and more viscous until it was of jellylike consistency and finally, after standing for from half an hour to 2 hours, it usually coagulated. In some cases it coagulated immediately after centrifuging. The following facts were noted:

(1) That fresh latex nearly always produces a liquid yellow fraction.
(2) That the chance of obtaining a coagulated yellow fraction or one with a porridgelike consistency increases the longer the latex is kept before centrifuging.
(3) That the yellow fraction is very unstable in that rapid or immediate coagulation can be brought about by gentle heating or dilution with water.

On exposure to air the yellow fraction darkened, but this discoloration did not occur in the original latex. When acid was added to the yellow fraction to a pH of about 4.9, as used in the preparation of crepe, the surface of the coagulum almost invariably became discolored to a very dark purplish-black. The coagulum of the original latex when treated in the same way, however, often did not discolor at all[6]. It was found that oxidizing enzymes were more active in the yellow fraction than in the latex, because inhibitors mostly remained in the white fraction.

Although the yellow fraction contains so many nonrubber components, it is possible to prepare crepe from it in the usual way. A remarkable property of these crepes is that they have a better resistance to the influence of direct sunlight than is the case with the normal crepes. A difference occurs also in favor of the yellow crepes when they are aged by heating (110° C), but this difference is not so striking.

PROPERTIES OF THE WHITE FRACTION

As a consequence of the withdrawal of the heavy yellow fraction with its high content of nonrubber components, the specific gravity and the content of the nonrubber components of the white fraction were lowered. The following properties were observed:

Specific gravity 0.966 (*cf.* 0.978)
Ash content 1.01 to 1.07 (*cf.* total solids)
N content 0.4 to 0.5% (*cf.* total solids)
Acetone extract 2.3% to 2.45% (*cf.* total solids)
Acid number of acetone extract 160 to 230

The dry rubber content and total solids proved to be about 20 per cent higher than those of the original latex. The pH (*c.* 6.8) of the white fraction was also higher than that of the latex.

Notwithstanding the higher dry rubber content the white fraction was distinctly less viscous than the original latex; viscosities of 13.9, 9.2, and 11.9 cp, against 16.8, 11.7, and 13.8 cp, respectively, were revealed.

The mechanical stability of the white fraction is lower than that of the latex, and the ammoniation increases the stability of the original latex to a greater extent than it does that of the white fraction. In other respects the white fraction is more stable than the original latex. With gentle heating in a waterbath it flocculates later and slower. Coagulation caused by the addition of acid begins later and proceeds more slowly than in the original latex. This is more marked after dilution, *e.g.*, to about 20 per cent dry rubber content.

White fraction latex creams faster and more efficiently than total latex,

giving a cream of a higher dry rubber content. (We have not yet been successful in creaming yellow fraction latex.) The improved creaming properties are connected with the lower viscosity of the white fraction latex[7], so that discarding the yellow fraction before creaming becomes an important factor in the improvement of the creaming efficiency of Hevea latex. We have already worked out a technical procedure to this effect[5].

Because of the removal of certain components which apparently have a protective action, white fraction latex is more sensitive to the action of zinc oxide than is total latex. In Kaysam mixtures, white fraction latex behaves like old total latex in that it gels very rapidly.

Finally, the white fraction is much less likely to coagulate spontaneously than latex; this phenomenon will be discussed later.

The following points of interest were established by the experiments.

(1) The white fraction never has any dark discoloration at its surface.
(2) Crepes prepared in the customary manner from the white fraction, which are naturally whiter than those of the original latex, are a little more susceptible to the effects of heat and sunlight.
(3) Films prepared from the white fraction are clear and transparent as glass.
(4) Microscopic investigation reveals in the white fraction latex no material other than rubber particles.

SPONTANEOUS COAGULATION

The spontaneous coagulation of field latex and the white and yellow fractions is strikingly different. The yellow fraction coagulates very soon after separation, in most cases within 2 hours, normal field latex after about 8 to 12 hours, while the white fraction may remain fluid for several days.

These phenomena are logically explained by the theory of Van Gils[8], which assumes that spontaneous coagulation is mainly due to the forming of salts of fat acids out of the lipoids of the latex. As the yellow fraction contains lipoids in a free state, *i.e.*, not dissolved in the rubber, it is consistent that this fraction should coagulate more rapidly. These phenomena cannot be explained completely by the action of bacteria, because these multiply abundantly in both the yellow and the white fractions.

DISCUSSION

Our investigations have shown that fresh latex of *Hevea brasiliensis* contains not only rubber particles and Frey-Wyssling's globules as independent substances, but that it also contains a considerable quantity of larger components, which on account of their more or less yellow color we have called lutoids. Their color is not sufficiently pronounced to show under the microscope, but it can be seen when they are separated *en masse* by centrifuging. Fundamentally these lutoids do not contain rubber, but because they easily stick together and form large entities, they nearly always enclose rubber particles and sometimes also Frey-Wyssling particles. Their presence in fresh unammoniated and undiluted latex is, when examined microscopically, very striking, and it is very remarkable that they have not been detected earlier. It seems that latex investigators in the past have given too much of their attention to ammoniated and diluted latex. Thus Frey-Wyssling found only the comparatively few and unimportant Frey-Wyssling's globules which do not dissolve by the addition of

ammonia. The sludge remaining in the bowl after centrifuging ammoniated latex consists partly of these Frey-Wyssling's globules and possibly also some undissolved remnants of the lutoids. From calculations based on the dry rubber content, total solids, and other data of the yellow fraction, it appears that the lutoids consist for the greater part (80 to 85 per cent) of water, whereas the dry material present consists of proteins, salts, and acetone solubles, etc., in the form of lipoids, and probably also sugars. This dry material represents 6 to 8 per cent of the total solids of the latex.

It is clear also why fresh unammoniated latex is much more viscous than ammoniated latex, because in the former the lutoids constitute a separate colloid dispersion which contributes to the viscosity of the system.

The process of fractional coagulation which is used in the manufacture of sole crepe is also explained. The dilution of the latex, the stirring, and the addition of a small quantity of acid are sufficient factors to agglomerate the lutoids until one big clot is formed, in which many rubber particles are enclosed. In fact, during our experiments we found that dilution and intensive stirring were sufficient to obtain the desired effect.

The importance of the lutoids is much greater than might be expected from their quantity. Our experiments are still progressing, and we have already established that much of the variability of the latex is due to these lutoids, the following factors being greatly influenced: mechanical and colloid stability, stability against spontaneous coagulation, viscosity and creaming capacity.

The intensity of the yellow color of the latex does not depend on the quantity of the lutoids but on their composition.

SUMMARY

Fresh *Hevea* latex is a complex system, containing two dispersed phases:

(1) rubber globules;

(2) lutoids, *i.e.*, small irregularly shaped, viscous colloidal bodies.

The lutoids dissolve in ammonia and other alkalies, coagulate when the latex is diluted with water but retain their form if the latex is diluted with salt solutions of certain concentrations.

By centrifuging, the lutoids are collected at the bottom of the tube as a separate layer with a sharp boundary. After separation, the fractions (now called the yellow and the white fractions) may be examined separately. Their properties are reviewed.

The importance of the lutoids for the general properties of the latex is discussed.

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ALTERATION OF NEOPRENE BY POLYMERIZATION TEMPERATURE *

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INTRODUCTION

The polymerization of 2-chloro-1, 3-butadiene (chloroprene) at different temperatures provides a range of polymers, in dry and latex form, that differ markedly in the raw state in their rate of crystallization and dispersion in solvents and in the physical properties of their vulcanizates. These polymers comprise Neoprenes that find wide application in industry, and a study of their structural differences forms a part of the general subject of the structure of polymeric substances.

Alterations of the properties of diene hydrocarbon polymers caused by such factors as the variation of the components of copolymers, the amount and nature of emulsifying agents and catalysts, the presence of modifying or regulating agents during polymerization, and the polymer yield are discussed by Starkweather and associates[1]. Investigations of the effect of the polymerization temperature have been more concerned with polymerization rate measurements than with changes in the physical properties of synthetic rubbers. Whitby and Crozier[2] studied the influence of polymerization temperature on the nature of dimeric products from isoprene and dimethylbutadiene. Considerable work, however, has been done on the change in properties with temperature of commercially available elastomers[3].

This paper describes representative effects of the polymerization temperature on the properties of polychloroprene, indicates how these variations furnish technical advantages, and outlines attempts to determine the structural differences that may account for the variation in properties.

DRY POLYMERS

Polychloroprene formed at 10° C quickly hardens or crystallizes, forms homogeneous solutions, and exhibits high tensile strength; whereas polymer produced at 100° C remains soft and flexible, only swells in solvents, and has low tensile strength. As the polymerization temperature is raised within these limits, the plasticity of the polymer decreases (Williams plasticity and recovery values increase), the resistance to stiffening increases, the solvent action of benzene diminishes, and the normal and hot tensile strength of the vulcanized polymer declines. This is illustrated in Tables I and II.

The T-10 and T-50 values show the relation between polymerization temperature and rate of stiffening of the vulcanizates at low temperatures. The T-10 value is characteristic of a given Neoprene compound, and remains essentially unchanged regardless of the state of vulcanization[4], while the T-50 temperature is customarily used to denote the state of vulcanization of an

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TABLE I

POLYMERIZATION TEMPERATURE EFFECT ON RAW POLYMER

Polymerization temperature (° C)	Polymer yield (% conversion)	Williams plasticity-recovery (inches ×10²)	Hardening at 25° C	Dispersion in benzene
10	93	55–0	Rapid (hours)	Complete
40	89	78–2	Slow (days)	Complete
55	94	120–60	Very slow (months)	Partial
100	74	195–100	None (2 years)	Swells only

TABLE II

POLYMERIZATION TEMPERATURE EFFECT ON POLYMER VULCANIZATES

Polymerization temperature (° C)	Tested at 25° C: Stress at 300% elongation (lbs./in.²)	Tested at 25° C: Tensile strength (lbs./in.²)	Tested at 25° C: Elongation (%)	Tested at 70° C: Tensile strength (lbs./in.²)	Tested at 70° C: Elongation (%)	Low temperature retraction (° C): T-10	Low temperature retraction (° C): T-50
10	3400	4950	530	2500	460	−14	+20
40	1920	4300	510	2050	450	−25	+ 2
55	1550	3600	620	1650	350	−30	−10
100	1600	2900	430	1200	240	−32	−21

Compounding formula: Neoprene 100, phenyl-beta-naphthylamine 2, light calcined magnesia 4, medium processing channel black 36, zinc oxide 5.
Vulcanized: 30 minutes at 141° C.

elastomer[5]. In this set of chloroprene polymers the increased rate of retraction denoted by the decreased T-50 value, together with the loss of plastic properties and increased resistance to swelling, suggests changes with polymerization temperature that are associated with vulcanization. However, the real change in the T-10 temperature implies a structural change during polymerization different from that occurring during vulcanization.

TABLE III

POLYMERIZATION TEMPERATURE EFFECT ON FABRIC ADHESION

Fabric assembly heated 10 minutes at 70° C before test

Polymerization temperature (° C)	Adhesion at 25° C (lbs./linear inch): After 15 min. at 25° C	Adhesion at 25° C (lbs./linear inch): After 24 hrs. at 25° C
10	10	34
40	5	6

The 40° C polymer represents in its hardening rate, dispersion in benzene, and stress-strain properties a general purpose Neoprene[6]. The rapid hardening of the polymer made at 10° C makes it especially suited for adhesive cements with a high initial bond strength, as shown in Table III.

EXPERIMENTAL

The polymerization recipe comprised chloroprene 100, N wood rosin 4, sulfur 0.6, water 150, sodium hydroxide 0.8, sodium salt of naphthalenesulfonic acid-formaldehyde condensation product 0.75, potassium persulfate 0.2 to 1.0. For polymerizations up to 55° C, the rosin and sulfur were dissolved in the chloro-

prene, and the solution was emulsified at the designated polymerization temperature in the water solution of the caustic, naphthalenesulfonic acid product, and persulfate by means of an Eppenbach Homo-mixer. Polymerization was carried out under nitrogen in a 2 liter round-bottom flask fitted with a glass stirrer, thermometer, and hydrometer tube[7]. In the case of the 55° C polymerization, the stirrer passed through a 70-mm. mercury seal, and the catalyst was withheld until after transferring the emulsion to the polymerizer.

For polymerizations at 100° C (boiling point of chloroprene is 59.4° C at 760 mm.) the ingredients of the polymerizing system were placed in a 3 × 38 cm. thick-walled Pyrex tube and emulsified by inverting the tube a number of times. The tube was closed with a Neoprene stopper that had been treated with caustic solution to remove extractable material. The tube was held in a perforated brass tube, to the cap of which was attached a 1 × 100 cm. bent metal rod that served as a handle by which the assembly could be plunged into a steam-heated water bath. About four minutes was required to obtain a polymer yield of 75 per cent at 100° C. The tube was then lifted from the hot bath and cooled at once in an ice-water mixture.

After polymerization, in all cases, the latex was treated with 2.5 parts of tetraethylthiuram disulfide per 100 parts of chloroprene as a plasticizing stabilizer[8]. The polymer was coagulated with a mixture of 10 per cent acetic acid and saturated sodium chloride solution, mill washed, and mill dried. The product contained the rosin, sulfur, and thiuram disulfide. Standard compounding and stress-strain testing procedures were followed. A modified T-50 test with the specimens racked 170 per cent was used[4].

The adhesion test-specimens were prepared as follows. Coatings of the polymer were applied as a 20 per cent benzene cement to give a polymer film about 0.1 mm. thick on one side of a 35.56 × 5.08 cm. (14 × 2 in.) strip of 10-oz. cotton duck, leaving about 2.54 cm. (1 in.) at each end uncoated for attaching the grips of the tester. The cement was allowed to dry until the surface was just tacky. Then the strip was doubled in half and bonded under a pressure of 300 lbs. per sq. in. applied for 10 seconds. After 24 hours aging at room temperature to evaporate completely the solvent, a 2.54 cm. × 15.24 cm. (1 × 6 in.) test-sample was died from the folded specimen. Just before testing, the sample was heated 10 minutes at 70° C to remove any hardening of the bonding film and allowed to cool at 25° C at least 15 minutes before measuring the bond strength. The bond strength was measured on a Model L6 Scott Tester, with a jaw separation of 5.08 cm. (2 in.) per minute.

LATEX POLYMERS

Although any polymerized emulsion may be referred to as a latex and the polymer dispersed therein regarded as a latex polymer, for the present purpose the designated latex polymers are those contained in latices that are prepared especially for making dipped goods, coatings, foam sponge, and the like. Owing to a low amount of regulator present during polymerization, the polymer in these latices, even when made at 20° C, is nonplastic and fails to disperse in solvents. But the freezing characteristics and the stress-strain properties of films made from these latices show the same variation with polymerization temperature as those of the plastic, dry polymers. As the polymerization temperature increases, the tensile strength at room temperature and at 70° C and the T-10 and T-50 values decrease. Representative results from compounded and vulcanized coagulated dip films from latices made at 20, 40, and 55° C are given in Table IV.

TABLE IV

POLYMERIZATION TEMPERATURE EFFECT ON LATEX FILM PROPERTIES

	Tested at 25° C			Tested at 70° C		
					Low temperature retraction (° C)	
Polymerization temperature (° C)	Stress at 600% elongation (lb./in.²)	Tensile strength (lb./in.²)	Elongation (%)	Tensile strength (lb./in.²)	T-10	T-50
20	1525	4450	850	625	−17	+17
40	990	3400	865	225	−20	+13
55	900	2350	770	100	−30	− 9

Compounding formula: polychloroprene in latex 100, clay 10, zinc oxide 5, phenyl beta naphthylamine 2. Vulcanized: 60 minutes at 140° C. Specimens racked 270% in T-50 test.

Other freeze-resistance tests that measure the rate of stiffening at low temperatures, *e.g.*, change in hardness, change in stiffness by Jolly balance deflection, and resistance to deformation, likewise show that the freeze resistance of latex polymers from chloroprene is increased as the polymerization temperature is raised.

The latex made at 40° C is a general purpose latex[9]. When properly compounded and vulcanized it yields films that do not stiffen with time at room temperature. The latex made at 20° C yields unvulcanized adhesive films which, similar to those of 10° C dry polymer, have a high initial strength, owing to freezing at ordinary temperatures. The 55° C latex yields vulcanized films, coatings, and other products that retain their flexibility at subzero temperatures. The freeze resistance at −10° C of a film of the 55° C latex polymer is compared in Figure 1 with the rapid stiffening of a film of 40° C latex polymer.

EXPERIMENTAL

The polymerization recipe for the latex polymers comprised chloroprene 94, N wood rosin 4, sulfur 0.25, water 100, sodium hydroxide 1.06, potassium persulfate 0.5, and, for the polymerization at 20° C, potassium ferricyanide 0.5 The emulsion preparation and polymerization procedure were the same as for the dry polymers. In each case the chloroprene was over 99 per cent polymerized, giving latices containing 50 per cent of solids.

The Jolly balance stiffening test (Figure 1) was performed as follows, with

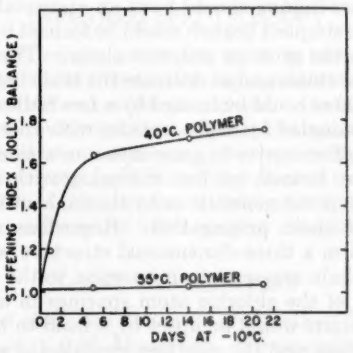

FIG. 1.—Effect of polymerization temperature on stiffening of latex films

portions of the latex films prepared for the tests in Table IV. Specimens 1.27 cm. × 6.35 cm. (0.5 × 2.5 in.) were cut from the latex films 0.5 mm. (0.020 in.) in thickness and in the center, 6.3 mm. (0.25 in.) from one end, one leg of a staple was attached parallel to the length of the specimen. The overhanging portion of the staple was opened to form a hook. The specimens were then fastened to a board with a second staple placed crosswise and exactly 5.08 cm. (2 in.) from the hook. The board with samples was placed in a cold box at $-10 \pm 0.5°$ C. A Jolly balance with a spring elongation of about 1 cm. per gram and sufficient chain, terminating in a hook, to reach the hooks on the specimens was placed over an opening in the cold box. A special index with lines spaced 1 cm. apart provided a means of measuring any change in the force necessary to raise the free end of a specimen a distance of 1 cm. as a result of stiffening during exposure to the cold atmosphere.

ANALYSIS OF POLYMERS

Attempts to determine the structural differences of polychloroprene made at different polymerization temperatures by ozonolysis, infrared spectroscopy, and *x*-ray diffraction reveal that these differences, although clearly evident in the variation of the polymer properties, are small in magnitude and difficult to detect by these analytical procedures.

The decreased rate of hardening or stiffening of the polymers is a pronounced effect of increased polymerization temperature. The rate of hardening is identified with the rate of crystallization or alignment of segments of the polymer chains[10]. It is postulated that irregularities in the polymer chain structure that would retard the crystallization are side vinyl or longer branching groups, cross-linking, head to head or tail to tail monomer addition, and *cis-trans*-isomerism. Variations in the polymer chain length are not regarded as having much influence on the crystallinity, since the region of crystalline orientation is very much smaller than the overall length of a single molecule[11]. Hunter and Oakes[12] did observe in polythene a tendency for the crystallites at any temperature to contain the larger molecules, and Richards[13] noted a decrease in crystallinity of polythene on adding low-molecular weight material, but in general the effect of molecular weight on crystallinity is small at high molecular weights. Although the polychloroprene made at 10° C has a higher molecular weight than that made at 40° C, fractions of the latter varying from 39,000 to 400,000 in molecular weight gave vulcanizates with the same T-10 value[14].

Branching and cross-linking should have an appreciable effect in retarding crystallization.[15] The simplest branch would be formed by 1, 2- or 3, 4-addition of a monomer unit to the growing polymer chain. This would interrupt the regular arrangement of atoms and so decrease the tendency to form a crystalline structure. Long branches could be formed by a free radical mechanism in which a growing chain is terminated by chain transfer with an existing polymer molecule, leaving a new active center to grow into a new side branch[16]. Branches and cross-links can be formed by free radical growth involving the double bonds in the polychloroprene molecule or by thermal activation of these double bonds independent of chain propagation. Regardless of the nature of the cross-linkages, they form a three-dimensional structure which offers resistance to the orientation of chain segments in proportion to the number of cross-linkages. The regularity of the chlorine atom spacings in a 1, 4- or head to tail addition of monomer units would be upset by a head to head (4, 1-1, 4) or tail to tail (1, 4–4, 1) addition, and the resulting irregularity would make alignment more difficult. With regard to the presence of varying amounts of mixed *cis-*

and *trans*-isomers in the same or different polymer chains, crystallites of all *cis*-polymer would not likely form, if the *cis*-configuration were present as a minor constituent; but the *cis*-structure would delay crystallization of the *trans*-isomer by creating an irregularity in the molecular structure.

OZONOLYSIS

Ozonolysis discloses that at least 94 per cent of the polychloroprene made at 10° and at 40° C is a 1, 4-addition product. This is based on the amount of succinic acid isolated from ozonized material.

The presence of appreciable side vinyl groups, longer side branches, and cross-linkages should be detected by the isolation and identification of polycarboxylic acids. Efforts to detect polycarboxylic acids in the ozonolysis products from these polymers have thus far been unfruitful. The 10° and 40° C polymers yielded only 0.06 and 0.05 per cent of formic acid, respectively, indicating no significant number of side vinyl groups.

In an analysis of GR-S samples by Rabjohn and coworkers[17] substantial amounts of tri- and tetracarboxylates were identified, and the accompanying volatile formic acid indicated the existence of 20 to 40 per cent of side vinyl groups in polymers of this type. From Neoprene and natural rubber, however, these workers obtained only small amounts of formic acid, which it is believed was formed by secondary oxidation. Oznolysis results of Klebanskiĭ and Chevychalova[18] revealed no significant structural differences between soluble chloroprene polymers prepared at 40° and 80° C. These workers found no evidence for a head-to-head structure in partially ozonized soluble polychloroprene.

In an experimental test case such a relatively highly cross-linked product at the omega or "popcorn" polychloroprene[19] gave approximately the same high amount of succinic acid by ozonolysis as the soluble plastic emulsion polymers, indicating that even in this highly insoluble, hard polymer the number of branches and cross-links is extremely small.

The polychloroprenes were ozonized in carbon tetrachloride solution at 0° C with a stream of oxygen containing about 2 per cent ozone. The ozonides were decomposed with hydrogen peroxide and the succinic acid determined by direct isolation. Samples of 10°, 40° C, and "popcorn" polymers yielded amounts of succinic acid corresponding to 93, 95, and 94 per cent respectively, 1,4-polychloroprene.

INFRARED SPECTROSCOPY

Infrared spectroscopy results are similar to those obtained by ozonolysis in revealing the 10° and 40° C polymers as having a general likeness and in showing no significant structural difference between them. Careful examination in the 3 micron region failed to reveal in either polymer the existence of vinyl groups[20].

Material for this analysis was prepared by repeatedly dissolving the polymers in benzene and precipitating with methyl alcohol to remove the nonpolymeric constituents. Films 25 microns in thickness were cast from benzene solutions on a mercury surface and lifted already attached to the spectrometer specimen holder.

X-RAY EXAMINATION

The identity period along the fiber axis of stretched films of 10° and 40° C polychloroprenes is 4.75 ± 0.08 Ångstroms, corresponding to a *trans*-2-chloro-2-butenylene unit structure[21]. No evidence for head to head or tail-to-tail

structure or for the presence of the *cis*-isomer has been obtained, but the presence of these configurations with a major portion of trans head-to-tail isomer cannot be excluded.

x-Ray diffraction patterns from a Norelco *x*-ray spectrometer equipped with a copper tube confirm that the varying rate of hardening of the chloroprene polymers produced at 10° and 40° C is associated with a varying rate of crystallization. They do not reveal the structural differences that affect the rate of crystallization; these polymers give the same patterns in the amorphous and crystalline states. The amorphous states are shown in Figure 2 by reproductions of the *x*-ray reflection intensities obtained before aging. The polymer made at 10° C attained the degree of crystallinity shown after aging only two days at 25° C, whereas the polymer foremd at 40° C required an aging period of 25 days before the crystallinity shown was obtained.

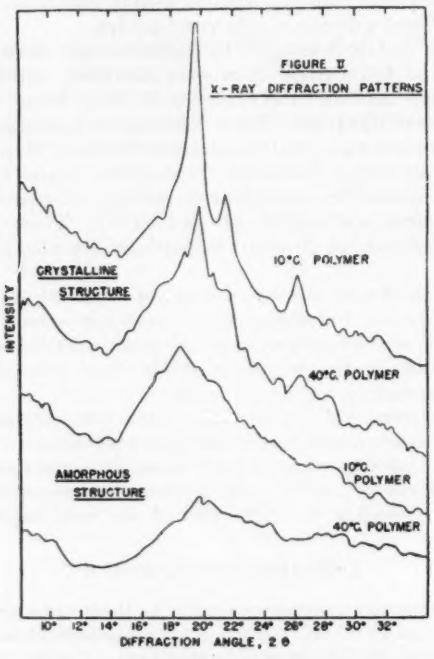

FIG. 2.—X-ray diffraction patterns.

The specimens measured 2 × 4 × 0.1 cm. mounted on a microscope slide. They were molded at 60° C, cooled in the mold before removal, and heated 20 minutes at 70° C before making the initial examination.

DISCUSSION OF RESULTS

The emulsion polymerization of a diene compound is a complex reaction and, although studied in considerable detail by Harkins and others[22], is not clearly understood. The interactions in the emulsion between the monomer, catalyst,

regulating agent, emulsifying agent, and water are of such a nature that a change in the concentration of any component proves to be a rate and a structure determining factor[1]. Temperature is another important element that can have a pronounced effect on the structure of the polymerization product.

The amounts of branching and cross-linking increase with increased polymerization temperature and decrease the plasticity and solubility of polychloroprene polymers. These factors also tend to decrease the tensile strength of vulcanizates[23]. Where the cross-linking is sufficient to render the polymer insoluble, it would be expected to decrease the rate of crystallization, as occurs in the case of rubber combined with varying amounts of sulfur[15]. In the soluble 10° and 40° C polymers less branching or cross-linking in the lower temperature product accounts for its higher plasticity (lower plasticity number), but may not be sufficient to give the difference in the rate of crystallization. The amount of branching and cross-linking in these polymers indicated by ozonolysis is less than 5 per cent and their solubility suggests it is much less than this. An influence of cross-linking is shown by the following: Neoprene produced at 10° C is soft and flexible when first isolated by freeze coagulation and air drying[24] and crystallizes to attain a Shore Type-A durometer hardness of 75 in about 32 hours at 25° C; after plasticization by milling the same polymer hardens to the same extent in 6 hours, owing to the mill breakdown of the cross-linked structure which retards the hardening of the unmilled material; unmilled and milled 40° C polymer shows the same effect, 25 and 5 days, respectively, being required to crystallize to the same extent as judged by the hardness increase.

A possible additional factor in crystallization is the existence of head-to-head or tail-to-tail structure or of intramolecular *cis*- and *trans*-configuration, with the irregular monomer addition or *cis*-isomer increasing with increased polymerization temperature. Lightly chlorinated Neoprene made at 10° or 40° C which contains irregularly spaced chlorine atoms is more resistant to crystallization than the unchlorinated polymer[14]. Polymer made at 55° C at a 75 per cent conversion and mill plasticized so that it is readily soluble (plasticity 54-0) undergoes little change in hardness when aged for several weeks, whereas a cross-linked, nonplastic film of latex polymer made at 20° C hardens in 3 days. Kemp and Straitiff[23] postulate that mixed *trans*- and *cis*-isomers must be present in Buna-S, and observed that mixed *cis*- and *trans*-isomers from rubber and gutta-percha give a somewhat lowered tensile strength. These workers were not certain whether this was a structural effect or failure to find the best cure. Evidence for mixed (1,4-1,4), (4,1-1,4), and (1,4-4,1) additions and for *cis*- *trans*-structures in polychloroprene is meagre at present, and the precise nature and amount of branching and cross-linking remain to be determined.

SUMMARY

Changes of the temperature at which 2-chloro-1,3-butadiene (chloroprene) is polymerized, with other variables held constant, gives Neoprenes with marked differences in the rate of crystallization and dispersion in solvents of the raw polymer and in the physical properties of the vulcanizates. For example, plastic polychloroprene formed at 10° C crystallizes quickly, forms homogeneous solutions, and exhibits high tensile strength; whereas polymer produced at 100° C fails to crystallize, only swells in solvents, and has low tensile strength. These changes in properties appear to be caused by alterations of the structure of the polymer, notably the side-branching, cross-linking, spacing of the chlorine atoms, and possibly *cis-trans*-isomerism. The structural differences are small

in magnitude and difficult to detect. Ozonolysis reveals that a soluble form of polychloroprene, as well as highly insoluble "popcorn" polymer, is at least 93 to 95 per cent 1,4-addition product and x-ray diffraction shows the polymer chains to have essentially a transconfiguration. Infrared spectroscopy indicates the absence of side vinyl groups. Branching and cross-linking explain the decreased rate of crystallization and other properties of the less soluble polymers, and it is considered that varying minor portions of 4,1-1,4 or 1,4-4,1 addition or of intramolecular *cis*-isomers are a factor in the crystallization of the soluble polymers. Technical advantages of the variations in Neoprene effected by polymerization temperature are outlined.

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REFRACTIVE INDEX OF NATURAL RUBBER FOR DIFFERENT WAVE LENGTHS *

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INTRODUCTION

Published values of the refractive index of natural rubber, with very few exceptions, have been concerned with the value at the wave length of the sodium D-lines (5893 Ångstrom units). This paper presents the results of measurements by the spectrometer method at this wave length and at four other wave lengths in the visible spectrum. Observations of the effect of temperature on the index are also made. The constants of several different types of dispersion equations are evaluated to obtain an equation to represent the data. The dispersion observed for rubber is compared with that of hydrocarbons of low molecular weight.

The experimental portion of this work was conducted in 1939, and some of the results have been presented in graphical form in a general paper by one of the present authors.[1] The war prevented further work on this problem until recently.

METHOD OF MEASUREMENT

The well known and conventional method of measurement of refractive index by observations of the angle of minimum deviation produced by a prism of known angle does not seem to have been previously applied to rubber. This very direct method commonly yields results of higher precision and accuracy than can be obtained by available commercial refractometers, since it is free from many of the complications and limitations inherent in comparison methods by critical-angle refractometry.

The rubber prisms required were made by molding the rubber between two plane glass plates inclined at an angle. A mold of 1-inch cold-rolled steel bars, fastened together by bolts, had an opening in which from one to six steel wedges could be placed, thereby fixing the angle of the prism at about 10° or some multiple of 10°. The rubber was molded against two glass plates, 20 × 10 × 3.5 mm., which were left in position after the molding. The glass plates were special "plane parallels", that is, they had faces which were plane and parallel to each other to within a few wave lengths of light, as evidenced by comparison with optical flats and by examination of the interference phenomenon known as Haidinger's rings. Since their faces were parallel, the collimated light beam in its passage through the glass underwent no deviation or dispersion, and the observed refraction was due entirely to the wedge of rubber between the plates.

The pale crepe rubber was milled only very slightly, a few passages through the warm rolls being found sufficient to make possible the production of a sheet about 1 cm. thick and relatively free from entrapped air. A specimen was cut

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very roughly to shape and inserted in the mold just described. The molding was performed in a steam vulcanizing press at a temperature of 150° C for about 30 minutes.

When the prism was placed on the spectrometer table, it was observed that the refracting angle showed a systematic change with time, a decrease of several minutes of angle a day being usually observed. This circumstance, arising no doubt from the plastic flow of the unvulcanized rubber, made it necessary to measure the prism angle before and after each set of measurements of the angle of deviation. The measurements of the refracting angle were made by means of reflections from the glass surfaces by the use of the spectrometer telescope, which was essentially autocollimating. As pointed out in a previous publication[2], the commonly used split beam method of measurement of refracting angle is never advisable. In the present instance additional difficulties would have arisen because of the finite thickness of the glass plates in contact with the rubber.

The spectrometer, which was manufactured by the Société Genevoise, has been described in detail in an earlier publication[3]. It has a circle 308 mm. in diameter and is graduated to 5-minute intervals. The use of micrometer microscopes made it possible to read angles to the nearest second.

The prism was set at the angle of minimum deviation in each case and the refractive index n computed from the usual spectrometer equation:

$$n = \frac{\sin \frac{1}{2}(A + D)}{\sin \frac{1}{2} A} \qquad (1)$$

where A is the refracting angle of the prism and D is the angle of minimum deviation.

The light sources used were a sodium arc, a hydrogen discharge tube, and a mercury vapor lamp. The wave lengths of the spectral lines utilized are as follows:

Wave length	Source	Designation
Ångstrom units		
6562.79	Hydrogen (alpha line)	C
5892.62	Sodium (weighted mean of two lines)	D
5460.74	Mercury	e
4861.33	Hydrogen (beta line)	F
4358.34	Mercury	g

The measurements with the g-line were made with more difficulty than those at longer wave lengths because of the greatly reduced transmission of light and the increased amount of light scattered by the sample in this region. Measurements of the transmission and scattering have been given in the earlier paper on the optical properties of rubber[1].

RESULTS

Table I gives the results of the measurements made with Prism 1, which had a refracting angle near 20°. More measurements were made with this prism than with any of several others, since it appeared to possess the best optical properties. Measurements were made at all five wave lengths, and a stirred air-bath in a water-jacketed constant-temperature prism housing equipped with a thermostat was employed to obtain values at 19.5° and 39.3° C. The temperatures could be measured to the nearest hundredth of a degree. At least 1 hour at any given temperature was allowed to elapse before readings of index were made.

The data shown in Table I for each wave length were treated by the methods of linear regression, or least squares, as outlined in books on statistical methods, for example, the text of Snedecor[4]. Inherent in this treatment is the usual assumption that there are no errors in the determination of the independent variable, in this case the temperature. By these methods values were obtained for the indices at 25° C, their standard deviations, and the rates of change of indices with temperature and their standard deviations.

TABLE I

DATA OBTAINED WITH PRISM 1

Date	Angle: Degrees	Minutes	Seconds	Temp. (° C)	n_C	n_D	n_e	n_F	n_g	$n_F - n_e$
7–17	20	55	25	28.7	1.51365	1.51737	—	1.52679	—	0.01314
7–18	20	52	15	28.0	1.51415	1.51793	—	1.52732	—	0.01317
7–18	20	52	2	28.5	1.51409	1.51782	—	—	—	—
7–19	20	50	24	28.4	1.51390	1.51765	—	1.52704	—	0.01314
7–19	20	50	26	28.5	1.51408	1.51773	—	1.52725	—	0.01317
7–19	20	50	17	28.7	1.51411	1.51781	—	1.52720	—	0.01309
9–2	20	39	48	28.4	1.51407	1.51793	1.52121	1.52727	1.53510	0.01320
9–5	20	39	30	26.5	1.51488	1.51868	1.52196	1.52809	1.53574	0.01321
9–5	20	39	37	27.1	1.51475	1.51850	1.52179	1.52790	1.53557	0.01315
9–6	20	39	31	26.9	1.51474	1.51847	1.52172	1.52791	1.53554	0.01317
9–7	20	45	52	39.3	1.51013	1.51385	1.51707	1.52324	1.53088	0.01311
9–7	20	45	52	39.3	1.51012	1.51382	1.51704	1.52318	1.53082	0.01306
9–11	20	34	45	19.5	1.51737	1.52113	1.52440	1.53062	1.53835	0.01325
9–11	20	34	45	19.5	1.51739	1.52111	1.52432	1.53066	1.53832	0.01327
Computed from above data at				25.0	1.515345	1.519093	1.522415	1.528536	1.536292	0.013193

Some observations were also made on Prism 2, a prism of less satisfactory optical quality than Prism 1. The results are shown in Table II. The second prism had a refracting angle near 10°, and of course did not produce so large an angle of deviation as did Prism 1. Observations were made with this prism for the sodium D-lines, the hydrogen C-line, and the hydrogen F-line only. The temperature range covered was likewise much smaller than previously.

TABLE II

DATA OBTAINED WITH PRISM 2

Date	Angle: Degrees	Minutes	Seconds	Temperature (degrees C)	n_e	n_D	n_F	$n_F - n_e$
7–22	9	58	16	28.2	1.51420	1.51792	1.52735	0.01315
7–24	9	58	3	29.0	1.51408	1.51779	1.52722	0.01314
7–25	9	57	59	29.0	1.51394	1.51766	1.52712	0.01318
8–17	10	4	35	32.3	1.51278	1.51647	1.52581	0.01303
8–18	10	4	48	32.3	1.51286	1.51660	1.52601	0.01315
8–18	10	4	47	32.3	1.51295	1.51659	1.52605	0.01310
8–28	10	2	56	28.2	1.51438	1.51806	1.52743	0.01305
8–30	10	2	36	27.2	1.51466	1.51836	1.52772	0.01306
8–31	10	2	19	26.5	1.51482	1.51860	1.52794	0.01312
Computed from above data at				25.0	1.515365	1.518095	1.528470	0.013117

Table III presents a comparison of the results obtained on the two prisms. As would be expected, the standard deviations obtained with Prism 2 are considerably larger than those found with Prism 1. In the last column ($n_F - n_e$) is shown as calculated from the individual observations shown in Tables I and II. The desirability of computing the difference in this manner is demonstrated by the fact that the standard deviations for it are considerably smaller than those for the indices at the individual wave lengths.

TABLE III

COMPARISON OF RESULTS OBTAINED WITH THE TWO DIFFERENT PRISMS

	C	D	e	F	g	(F−C)*
Index n^{25} for Prism 1	1.515345	1.519093	1.522415	1.528536	1.536292	0.013193
Standard deviation of n^{25} (Prism 1)	37.4×10^{-6}	35.2×10^{-6}	63.6×10^{-6}	43.2×10^{-6}	49.3×10^{-6}	10.5×10^{-6}
Index n^{25} for Prism 2	1.515365	1.519095	—	1.528470		0.013117
Standard deviation of n^{25} (Prism 2)	94.8×10^{-6}	152×10^{-6}	—	147×10^{-6}	—	42.5×10^{-6}
Difference between indices of Prism 2 and Prism 1	20×10^{-6}	2×10^{-6}	—	-66×10^{-6}	—	-76×10^{-6}
dn/dT for Prism 1	-367.7×10^{-6}	-369.9×10^{-6}	-370.1×10^{-6}	-376.5×10^{-6}	-378.2×10^{-6}	-8.8×10^{-6}
Standard deviation of dn/dT for Prism 1	5.90×10^{-6}	5.54×10^{-6}	8.11×10^{-6}	6.62×10^{-6}	6.29×10^{-6}	1.6×10^{-6}
dn/dT for Prism 2	-341×10^{-6}	-345×10^{-6}	—	-340×10^{-6}	—	-1.8×10^{-5}
Standard deviation of dn/dT for Prism 2	19.2×10^{-6}	30.7×10^{-6}	—	29.7×10^{-6}	—	8.6×10^{-6}
Difference between values of dn/dT of Prism 2 and Prism 1	$+26.7\times10^{-6}$	$+24.9\times10^{-6}$	—	$+36.5\times10^{-6}$	—	$+7.0\times10^{-5}$

* The values in this column have been calculated directly from the observations shown in Table I and Table II, and are not obtained from differences of preceding columns of Table III.

The differences between the values of index at each wave length for the two prisms can be seen to be of no significance when they are compared with the standard deviations. The differences are less than the standard deviation of Prism 2 for each of the three spectral lines, and even for ($n_F - n_C$) the difference is less than twice the standard deviation. Similarly, the differences in dn/dT are not significant, since they are less than twice the standard deviation.

Since the precision of the values obtained with Prism 1 was much greater than that obtained with Prism 2 and more observations were made with it, the remainder of the paper will be concerned only with the values obtained on Prism 1.

It should be clearly recognized that the present work does not include a study of the dependence of refractive index on composition. The rubber used to make the second prism probably came from the same bale as that used to make the first. For simplicity, the results have been treated as if the sample were pure rubber hydrocarbon, whereas it is only 93–94 per cent hydrocarbon and is known to contain resins in solution and proteins, salts, and other foreign substances dispersed in it. Hence the number of significant figures used here shows only the precision of the present measurements on a sample of given composition. Earlier work[5] has shown little variation with composition in the fourth-place index values, but further studies would be required to show the effect of impurities on fifth-place and sixth-place values.

DISCUSSION

The results of measurements of refractive index for the D-line have been summarized in an earlier paper.[6] The most reliable value of n_D^{25} was judged to be 1.5190, found by McPherson and Cummings[7]. This is in very good agreement with that found in the present work, namely, 1.519093.

McPherson and Cummings also made measurements with a Pulfrich refractometer, and reported an exceedingly large value for the dispersion, $n_F - n_C$. In the course of the present work the original data of McPherson and Cummings were reëxamined, and it was discovered that, on account of a clerical error, incorrect values were given for the refractive index of the F-line and consequently for the dispersion. The corrected results of McPherson and Cummings are as follows:

Temperature	24.5° C	25.0° C
n_C	1.5153	1.5151
n_D	1.5190	1.5188
n_F	1.5283	1.5281
n_F—n_C	0.0130	0.0130

These values are lower than those given in the present work by 2 to 4 units in the fourth decimal place.

A summary of previous values of the rate of change of index (D-line) with temperature is as follows:

Author	Year	dn/dT
McPherson[8]	1932	360 $\times 10^{-6}$
Kirchhof[9]	1932	369 $\times 10^{-6}$
McPherson and Cummings[7]	1935	350 $\times 10^{-6}$
Present work	—	369.9 $\times 10^{-6}$

In a previous publication[6] it has been shown that the empirical Eykman equation, $(n^2 - 1)/(n + 0.4) = Rd$, where d is the density and R a constant,

can be differentiated to yield the following equation:

$$\frac{dn}{dT} = -\frac{1}{\frac{2n}{n^2-1} - \frac{1}{n+0.4}}\left(\frac{1}{V}\frac{dV}{dT}\right) \qquad (2)$$

Here V is the volume of a given mass of the material, so that $(1/V)\ (dV/dT)$ is its volume expansivity. It has now been found that the coefficient by which the expansivity is multiplied in the right-hand member of this equation can be represented to within about 0.2 per cent over the complete range of normal refractive indices, namely from 1.33 to 1.7, by the expression $(1.10440n - 1.12226)$. Thus the equation becomes

$$\frac{dn}{dT} = -\ (1.10440n - 1.12226)\left(\frac{1}{V}\frac{dV}{dT}\right). \qquad (3)$$

Of the three observable quantities involved in this equation, it is considered that the experimental uncertainty is greatest in the value of the expansivity. Consequently the expansivity has been calculated from the optical data by taking the ratio of $(dn/d\mathrm{T})$ to $(1.10440n - 1.12226)$ for each of the spectral lines. The following results were obtained:

Spectral line	Calculated expansivity
C	667×10^{-6}
D	666×10^{-6}
e	662×10^{-6}
F	665×10^{-6}
g	658×10^{-6}

The mean value, 664×10^{-6} (deg. C)$^{-1}$, is in excellent agreement with values directly observed[10].

By inserting this mean value for the expansivity and the value for n^{25} in equation (3) one then has:

$$dn/dT = -\ (1.10440n^{25} - 1.12226)\ (664 \times 10^{-6}) \qquad (4)$$

The values of the right-hand member of this equation are compared with dn/dT as directly observed in the following tabulation:

	dn/dT		
Spectral line	Calculated	Observed	Difference
C	366.1×10^{-6}	367.7×10^{-6}	-1.6×10^{-6}
D	368.8×10^{-6}	369.9×10^{-6}	-1.1×10^{-6}
e	371.2×10^{-6}	370.1×10^{-6}	$+1.1\times10^{-6}$
F	375.7×10^{-6}	376.5×10^{-6}	-0.8×10^{-6}
g	381.4×10^{-6}	378.2×10^{-6}	$+3.2\times10^{-6}$

The agreement is very satisfactory.

The molecular refractivity can be calculated by the Lorenz-Lorentz relation from the present data by taking the value 0.906 g. per cc. for the density at 25° C of purified natural rubber[11]. As pointed out in the earlier paper[1], the result, 22.82, is in sufficiently good agreement with values obtained by taking the sum of atomic refractivities to afford optical confirmation of the existence of a C_5H_8 group containing one double bond as the unit group in rubber. It would be desirable to apply the methods outlined by Taylor, Pignocco, and Rossini[12] to a more detailed study of the data given in the present paper.

COMPARISON OF REFRACTIVITY INTERCEPT AND SPECIFIC DISPERSION WITH VALUES FOR OTHER HYDROCARBONS

The refractivity intercept, $n_D - d/2$, and specific dispersion, $10^4\ (n_F - n_C)/d$, where d is the density, have been used for some years to distinguish between different classes of hydrocarbons[13]. Values for these quantities applicable to hydrocarbons with not more than nine carbon atoms have been given by Rossini and coworkers[14]. The lowest and the highest values found for each class of hydrocarbon, together with the mean of the two, are listed in Table IV for comparison with the refractivity intercept and the specific dispersion for rubber. In these computations the value 0.906 g. per cc. has again been used as the density at 25° C of purified natural rubber.

TABLE IV

COMPARISON OF VALUES OF REFRACTIVITY INTERCEPT AND SPECIFIC DISPERSION WITH THOSE FOUND IN N.B.S. CIRCULAR C.461 "SELECTED VALUES OF PROPERTIES OF HYDROCARBONS," BY ROSSINI AND CO-WORKERS [14]

	Refractivity intercept $n_D^{25} - d/2$			Specific dispersion $10^4\ (n_F^{25} - n_C^{25})/d$		
Paraffins	Low	High	Mean *	Low	High	Mean *
C_5H_{12}	1.0436	1.0441	1.04385	98	99	98.5
C_6H_{14}	1.0437	1.0448	1.04425	97	100	98.5
C_7H_{16}	1.0439	1.0454	1.04465	96	100	98
C_8H_{18}	1.0437	1.0458	1.04475	96	100	98
C_9H_{20}	1.0420	1.0470	1.0445	94	101	97.5
Monoolefins						
C_5H_{10}	1.050	1.056	1.053	128	135	131.5
C_6H_{12}	1.049	1.058	1.0535	122	132	127
C_7H_{14}	1.048	1.057	1.0525	118	130	124
C_8H_{16}	1.050	1.055	1.0525	116	127	121.5
Diolefins with Conjugated Double Bonds						
C_5H_8	1.080	1.091	1.0855	255	225	225
C_6H_{10}	1.075	1.091	1.083	225	225	225
Diolefins with Adjacent Double Bonds						
C_5H_8	1.06	1.074	1.067	—	—	—
C_6H_{10}	1.054	1.069	1.0615	—	—	—
Other Diolefins						
C_5H_8	1.057	1.057	1.057	—	—	—
C_6H_{10}	1.057	1.062	1.0595	—	—	—
Rubber †$(C_5H_8)_p$	—	—	1.066	—	—	145.6

* Mean of low and high values.
† The number of (C_5H_8)—units, or degree of polymerization is denoted by p.

From the comparison shown in Table IV one can see that both the refractivity intercept and specific dispersion of rubber are somewhat above the corresponding values for the monoölefins, but not nearly as high as those for the diolefins with conjugated double bonds. This is exactly what would be expected from the structure of the rubber polymer. The double bonds in rubber are separated by four skeletal carbon atoms rather than by two carbon atoms as in a conjugated system. It has already been suggested[15] that this fact gives rise to a slight degree of double bond character in the single bond half-way between two double bonds.

DISPERSION EQUATIONS

From the data obtained in the present work it is possible to calculate the constants in a dispersion equation, which gives the relation between refractive index and wave length. From a consideration of standard deviations, one can draw conclusions regarding the validity of a particular form of dispersion equation. The present work shows that neither the Cauchy dispersion equation nor the Sellmeier dispersion equation is adequate to represent the observed data if the number of parameters is limited to two.

The two-constant Cauchy dispersion equation[11] is usually written:

$$n = A_1 + B_1/\lambda^2 = A_1 + B_1 \nu^2 \tag{5}$$

Here n is the refractive index, λ is the wave length, and ν its reciprocal, the wave-number of the light. A_1 and B_1 are constants characteristic of the medium.

The constants in the Cauchy equation were evaluated at the five different wave lengths from the index for Prism 1 by the usual methods of linear regression. The following equation was thus obtained:

$$n = 1.498648 + 71.16 \times 10^{-6}/\lambda^2 \tag{6}$$

A comparison of observed values with those calculated from this equation is given in Table V. It will be seen that the differences are considerably larger than the corresponding standard deviations of the observations. The observed variance in the Cauchy equation values yields a standard deviation of 176×10^{-6}, which can be compared with the average standard deviation of an observed value, namely, 46×10^{-6}. Consequently, it is concluded that the Cauchy dispersion equation with two parameters does not adequately represent the observations.

The single-term Sellmeier dispersion equation[11] is usually written:

$$n^2 - 1 = C/(\nu_0^2 - \nu^2) \tag{7}$$

where C and ν_0 are constants. For purposes of calculation this equation may be written in the following form:

$$1/(n^2 - 1) = A_2 + B_2 \nu^2 \tag{8}$$

The constants have been evaluated from the index values for Prism 1, to yield the following equation:

$$1/(n^2 - 1) = 0.800139 - 123.09 \times 10^{-12} \nu^2 \tag{9}$$

Table V also shows the comparison of observed values with those calculated from this equation. It will be noted that the representation of the data is still

TABLE V

COMPARISON OF TWO-CONSTANT DISPERSION EQUATIONS

	C	D	e	F	g	F−C
Observed value n^{25}	1.515345	1.519093	1.522415	1.528536	1.536292	0.013193
Standard deviation	37.4×10^{-6}	35.2×10^{-6}	63.6×10^{-6}	43.2×10^{-6}	49.3×10^{-6}	10.5×10^{-6}
Calculated from Cauchy equation	1.515169	1.519138	1.522510	1.528757	1.536108	0.013588
Difference between observed and calculated values	$+176 \times 10^{-6}$	-45×10^{-6}	-95×10^{-6}	-221×10^{-6}	$+184 \times 10^{-6}$	-395×10^{-6}
Calculated from Sellmeier equation	1.515281	1.519116	1.522420	1.528660	1.536202	0.013379
Difference between observed and calculated values	$+64 \times 10^{-6}$	-23×10^{-6}	-5×10^{-6}	-124×10^{-6}	$+90 \times 10^{-6}$	-186×10^{-6}

TABLE VI

"BEST" VALUES RESULTING FROM PRESENT INVESTIGATION

	C	D	e	F	g	F−C
n^{25}	1.515345	1.519093	1.522415	1.528536	1.536292	0.013193
Standard deviation	37.4×10^{-6}	35.2×10^{-6}	63.6×10^{-6}	43.2×10^{-6}	49.3×10^{-6}	10.5×10^{-6}
of n^{25} dn/dT	-367.7×10^{-6}	-369.9×10^{-6}	-370.1×10^{-6}	-376.5×10^{-6}	-378.2×10^{-6}	-8.8×10^{-6}
Standard deviation of dn/dT	5.90×10^{-6}	5.54×10^{-6}	8.11×10^{-6}	6.62×10^{-6}	6.29×10^{-6}	1.6×10^{-6}

not adequate, although the differences and standard deviations associated with the Sellmeier equation are appreciably less than the corresponding values associated with the Cauchy equation. The standard deviation associated with the variance shown in the table is 84×10^{-6}.

The corresponding Lorenz dispersion equation, which is quite similar to the Sellmeier form, is as follows:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{C_2}{\nu_0^2 - \nu^2} \tag{10}$$

Preliminary calculations indicated that it did not represent the data as well as the Sellmeier equation. Consequently, it was not considered further.

The equations thus far presented have been two-constant equations. In no previous case with which we are familiar has a two-constant equation been adequate to express the dispersion shown by fifth-place refractive index measurements. A three-constant equation may be successful for some materials, but most of them require a four-constant equation. However, it has not been found necessary to go beyond a four-constant equation. Such an equation, for example, has been shown to be quite adequate to represent the sixth-place index values obtained in the highest precision measurements on water[16]. The Ketteler-Helmholtz equation has a theoretical justification more satisfactory than that behind the simpler equations, and probably should be used for the calculation of index at wave lengths other than those given here.

CONCLUSIONS

The refractive index of natural rubber and its variation with temperature and wave length are those which would be predicted for a similar hydrocarbon of low molecular weight. A two-constant equation of the Cauchy or Sellmeier type is inadequate to express the relation between refractive index and wave length for rubber.

For convenient reference the best values resulting from the present investigation are recapitulated in Table VI.

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THE LOW-TEMPERATURE PERFORMANCE OF BUTYL INNER TUBES *

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INTRODUCTION

Butyl was adopted as the preferred material for inner tubes in the synthetic rubber program, and this decision was later justified by the following production experience.

(1) Growth rates of Butyl tubes in hot weather service are lower than those of natural rubber tubes[1].
(2) Restriction of the percentage unsaturation to that needed for vulcanization gives tubes with improved aging resistance. Practical outcomes of this are maintenance of high tear resistance, even after prolonged service, and slow rate of leakage after puncturing.
(3) Air-holding ability is eight to ten times better than natural rubber, which indirectly contributes to longer mileage records for the tires in which such tubes are used[1].
(4) The unvulcanized compounds are relatively insensitive to variations in mechanical working, which ensures maintenance of uniform raw stock viscosity.

In the spring of 1945, however, reports received through the Inner Tube Subcommittee of the Canadian Tire Manufacturers' Committee, concerning the first year's commercial experience in Canada with Butyl inner tubes, revealed failures experienced with passenger car tubes mounted and operated during winter months in Canada at temperatures of zero to −20° F. No difficulties were experienced with bicycle tubes, or with bus and truck sizes which were operated at higher pressures, and it appeared that even in the passenger car sizes, failures could be prevented by operating with tire pressures over 30 lbs. per sq. in.

Since buckling and inside chafing of Butyl tubes occurs only to an appreciable extent in continued service at subzero temperatures, it can be realized that the temperature limitations on Butyl tubes are not of consideration in such climates as are encountered in the greater part of Europe, South America, and the United States. They are of considerable importance in Canada, however, where winter temperatures of −20° F are not uncommon. Investigation of the problem has consequently been of prime concern to the Polymer Corporation, operators of the Canadian Butyl Plant at Sarnia, Ontario, working in coöperation with the Standard Oil Development Co. and the Canadian Rubber Companies, through the Inner Tube Subcommittee of the Tire Technical Committee. During 1946 the cold room facilities of General Motors, Oshawa, Ontario, were utilized for testing purposes until, on April 7, 1947, construction was com-

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pleted and operation commenced of a fully equipped cold room at the Polymer Corporation, Ltd., plant. At the same time, continuous pilot plant equipment was installed for preparation of experimental polymers.

When returned tubes were cut open and examined closely, evidence was found of numerous folds in the crown area, usually parallel to the circumference, and V-shaped chafing starting from inside the tube. Experiments conducted with tire and tube assemblies running on a 4-ft. diameter drum at temperatures down to −20° F revealed that buckling could not be induced by continuous operation, but was best demonstrated by a cyclic procedure, with alternate 30 minutes running, followed by 30 minutes resting[2]. From the multiplicity and faintness of the buckles, it was deduced that they were of fugitive nature and often disappeared as temperatures were attained, either by flex friction or atmospheric conditions, at which Butyl regained normal resiliency.

Subsequent experiments indicated that theories to explain formation of buckles based on air entrapped between tire and casing could be ruled out, that any procedure which led to a slight degree of tack between casing and tube, such as use of casing dope or absolutely clean tubes and casings, largely eliminated buckling and that casing lubricants such as talc or soapstone used to reduce sticking and facilitate mounting accentuated the trouble. In view of previously published data on the low-temperature properties of elastomers[3], it was concluded that buckling was associated with the loss of resilience of Butyl at low temperatures. It is now believed that compression of the crown region of the inner tube occurs at the area of contact of the tire with the road while at the same time extension takes place of the portion of the tube adjacent to the sidewall. At low temperatures it is believed that these strains are not relieved as the wheel rotates, but accumulate until buckling occurs. After serious buckling has occurred, the air pressure and the friction between the tube and casing often prevent the fold from being extricated; nevertheless, this is not a growth effect, since the tube recovers after the pressure is released. As mentioned above, a small degree of friction may prevent a buckle from forming; to eliminate minor variations in test work due to these causes, all tubes evaluated at Sarnia have been mounted with excess talc lubrication between tube and casing.

Studies by Mullins[4] have shown that curves showing the relation between rebound resilience, determined by the falling ball method, and temperature for natural rubber and synthetic types have well defined minima at low temperatures. Resilience was shown to decrease with increasing degree of black loading, although the value of the minimum resilience and its corresponding temperature were not affected. On the other hand, incorporation of increasing quantities of dioctyl phthalate as plasticizer shifted the minima to lower temperatures, and therefore extended the temperature range of rubberlike elasticity.

It appeared, therefore, that a promising line of investigation was to develop a Butyl type of formulation containing high percentages of inexpensive plasticizers. Since standard Butyl, with a Mooney specification range of 40 to 50, can only accommodate up to 12 parts plasticizer per 100 parts rubber, which is not sufficient to effect significant improvement, conditions were developed in the Butyl plant for producing a processable type of polymer with a Mooney specification range of 70 to 80, designated as GR-I R-13. This material permitted use of up to 25 parts of plasticizer and demonstrated definite improvement in low-temperature performance in the cold room.

The work described in this report includes studies of the effect of various operating conditions, such as temperature, tire deflection, casing composition,

and acceleration on the incidence of buckling in plasticized R-13 type tubes in an accelerated cold room test, summarizes experiments designed to minimize chafing after buckling has occurred, and presents laboratory correlations of various physical properties with inner tube performance.

PROCEDURES

The cold room at the Polymer Corporation, Ltd., consists essentially of an insulated room, 23 × 16 × 11 ft. high, refrigerated by a controlled ethylene coolant system installed above a false ceiling in the room, with a forced circulation of air by two rotary fans. Two 4-ft. diameter steel drums are inset in the floor of the cold room on a single shaft extending through the wall to an outside control room. The shaft is driven at a speed of 272 r.p.m. (38.8 m.p.h. on the drum surface) by a V-belt drive and hydraulic coupling from a 60 h.p., 1770 r.p.m., A.C. motor. The tube-tire assemblies are mounted on steel I-beam frames located so that two sets of tires revolve on each drum. Adjustable weights on the beams provide that a load of 915 pounds acts vertically at the point of contact of the tire and drum. This load represents 115 per cent overload for normal pressure conditions according to Tire and Rim Association data for 600 × 16, 4-ply casings operated at 20 lbs. per sq. in.

A cyclic method of testing was developed, consisting of soaking the assembly under load at the cold room temperature for 30 minutes, accelerating to 38.8 m.p.h. in a given time, running at this speed for 15 minutes, and repeating the above steps. In the data reported herein, the temperature, inflation pressure, and acceleration alone were varied. The accelerations investigated, namely 10 seconds, 40 seconds, and slow, were obtained by varying the starting position of the hydraulic coupling clutch lever and the time at which the clutch lever was engaged after the drive motor was started. With the 10-second acceleration, the speed was increased linearly to 38.8 m.p.h. in 10 seconds. With the 40-second acceleration, full speed was attained in 40 seconds. The slow acceleration was designed to result in a step in the acceleration curve at approximately

TABLE I

RAW POLYMER SPECIFICATIONS

	GR-I 50	GR-I 15	R-13
Chemical			
Volatile matter (heat loss)	0.30 max.	0.30 max.	0.30 max.
Ash	0.75 max.	0.75 max.	0.75 max.
Stabilizer	0.10 max.	0.10 max.	none added
Physical			
Viscosity (ML 212° F at 8 min.)	40 min.	40 min.	70 min.
	50 max.	50 max.	80 max.
Properties of vulcanizates at 82° F			
Tensile strength (lb. per sq. in.)			
40 min. cure at 307° F	2500 min.	2400 min.	2500 min.
Ultimate elongation			
40 min. cure at 307° F	650% min.	550% min.	650% min.
Modulus at 400% elongation (lb. per sq. in.)			
20 min. cure at 307° F	575 min.	750 min.	575 min.
	775 max.	950 max.	775 max.
40 min. cure at 307° F	875 min.	1125 min.	875 min.
	1125 max.	1375 max.	1125 max.
80 min. cure at 307° F	1200 min.	1475 min.	1200 min.
	1500 max.	1775 max.	1500 max.

TABLE II

TUBE FORMULATIONS

	GR-I 15 Control	F-I	F-III	F-VIII	F-XV
GR-I 15		—	—	—	—
GR-I R-13		100.0	100.0	100.0	100.0
PBN		0.25	0.25	0.4	0.25
Zinc oxide		5.0	5.0	5.0	5.0
SRF black		35.0	35.0	—	—
HMF black	Current	15.0	15.0	—	—
Kosmos-20 (SFR)	Commerical	—	—	—	35.0
Philblack-A (HMF)	Formulation	—	—	15.0	15.0
Gastex		—	—	35.0	—
Tuads		1.0	1.0	1.0	1.0
Captax		0.5	0.5	—	0.5
Sulfur		2.0	2.0	2.0	2.0
Plasticizer oil		25.0	20.0	25.0	25.0
		183.75	178.75	183.4	183.75

TABLE III

PLASTICIZER PHYSICAL DATA

Oil	Description*	Specific gravity	Flash point (° F)	Pour point (° F)	Viscosity at 80° F (centipoises)	VI..
Trioctyl phosphate (TOF)		0.901	—	—	15	80.0
Galena CC-10W	Naphthenic base, phenol treated	0.872	350	−35	37	26.7
Barosa 43		0.866	410		44	105.7
Polar 45		0.878	375	−25	76	85.0
Frigol 50		0.876	415	−25	104	69.6
Forum 56	Paraffin base, acid treated	0.904	—	—	158	70.4
DB-61	MCL, phenol treated	0.882	—	—	177	95.0
Circosol 2XH		0.944	—	—	1390	95.0
Indonex 634½		0.998	460	+40	5460	—
Dutrex 6		1.01	—	—	21000	—
Indonex 639½		1.02	520	+75	265600	—
Indopol H-300	Low molecular weight polybutene	0.894	505	+35	51000	—

* All but TOF and Indopol H-300 are hydrocarbon oils; Indopol is a low-molecular-weight polybutene.

half speed or at 30 seconds time, simulating a gear shift under road conditions. Full speed of 38.8 m.p.h. was not attained until approximately 100 seconds with this technique.

Testing is carried out continuously to chafing failure, the extent of buckling being followed daily by *x*-ray fluoroscopic scanning and photographic plates in certain cases. The *x*-ray equipment was obtained from the Victor X-Ray Corporation, and is operated at 80,000 volts, 5 milliamperes.

The various experimental inner tubes were obtained through the coöperation of the Canadian industry. The control tubes and the majority of the tires were obtained from retail stock. Specifications of the polymers involved in this study appear in Table I, and the tube compounds in Table II. The physical data of the plasticizers investigated appear in Table III.

LABORATORY METHODS

Viscosity.—Absolute viscosity of plasticizers was determined with a Brookfield Synchro-Lectric viscometer, which utilizes measurement of the torque on a spindle rotating at a definite constant speed while immersed in the material under test. The viscosities reported here were obtained at 80° F. The viscosity index was calculated from kinematic viscosity values in centistokes determined at 100° and 210° F, using Ubbelohde viscometer tubes.

Plasticizer loss.—(1) Volatile loss test: Plasticizer loss due to volatilization was determined for 2-in. diameter × 0.075-in. discs heated in a circulating air oven for 168 hours, maintained at 150° ± 1° F.

(2) Pressure differential test: This test was developed to provide a measure of the losses from specimens under pressure as might be encountered in actual service. A carefully weighed press-cured slab (6 × 6 × 0.075 in.) of plasticized Butyl stock is placed over the open face of a small pressure vessel and backed by a similar slab of natural rubber tube stock supported by a 16-mesh screen. A flange is bolted to the vessel to hold this assembly in place, 30 lbs. per sq in. air pressure imposed on the pressure chamber and the apparatus placed in a vulcanizer at atmospheric pressure, maintained at 150° F. After 168 hours the assembly is dismounted and the plasticized Butyl slab reweighed.

Low-temperature modulus function.—A laboratory method incorporating retraction rate and retractive stress was developed by the Standard Oil Development Co., which, applied to inner tube performance, provided an index of buckling[5]. The simplest expression relating elastic (reversible) modulus M_e and viscous (irreversible) modulus M_v is as follows:

$$M = M_e + M_v$$

where M = total modulus.

Values of M and M_e at −10° F are determined experimentally, using a micro Scott tester or a modified hot-Scott tester, thus enabling M_v to be calculated by difference. An empirical expression was derived which gave greater weight to the retractive stress term $\frac{(1)}{(M_e)}$ than to the ratio of M_v to M_e which provides an index of retraction rate.

$$\text{Buckling tendency } (1/k) = \frac{1}{M_e}\sqrt{\frac{M_v}{M_e}}$$

Rebound.—The rebound resilience measurements were obtained on an instrument made in these laboratories, utilizing the falling ball method, in which the height of rebound is recorded on a photographic plate. A steel bearing ball, 0.5 inch diameter, weighing 13.9 grams, falls through 24.5 inches onto the surface of a Goodyear-Healey rebound block. The sample is totally immersed in a cooling liquid for a definite period of time; the liquid level is slightly lowered so that the block surface is just free of the liquid, and the ball is dropped immediately. The height of rebound is measured from a photographic negative on which the path of the ball is recorded. The Standard Goodyear Healey Rebound test was used for the resilience determinations at 82° F.

Retraction rate.—The retraction rate of the various Butyl stocks was measured by means of a modified T-50 test procedure. The R-30 value is the time in seconds required for a T-50 dumb-bell (2 inches between shoulders) to retract from 150 per cent to 75 per cent extension at −30° F. The determinations were made using a T-50 apparatus made by the Henry L. Scott Co.

RESULTS

(1) *Effect of casing composition, tire pressure, and acceleration.*—Table IV shows comparisons of performance at −10° F in the cold test-room of tubes made from a standard GR-I 15 composition and plasticized GR-I R-13 types in casings containing 23 and 67 per cent natural rubber, operated at 19 and 24 lbs. per sq. in. initial pressure. It will be seen that the plasticized tubes have at least five times the life of standard tubes and that the most important operating variable adversely affecting performance of both standard and plasticized tubes is reduction in tire pressure, which causes increased deflection under load.

TABLE IV

EFFECT OF ACCELERATION AND DEFLECTION ON PERFORMANCE

Test Conditions:
Cycle: 15-minute, run, 30-minute soak
Wind velocity: 20 m.p.h.
Temperature: −10° F
Running speed: 38.8 m.p.h.
Miles per cycle: 9.6
Cycles per day: about 30.
Drum diameter: 4 ft.
Mounting procedure: talc

Inner tube type	Casing type	Acceleration type	Initial pressure (lb. per sq. in.) gauge	Static deflection (in.)	No. of tests	Number of cycles to incidence of buckling	Number of cycles to chafing failure
Control	23%	10 sec.	19	$12\frac{42}{64}$	3	<17	27
F-III	23%	10 sec.	19	$12\frac{42}{64}$	2	55	>101
Control	67%	10 sec.	19	$13\frac{1}{64}$	2	<10	29
F-VIII	67%	10 sec.	19	$13\frac{1}{64}$	3	56	200
Control	67%	slow	19	$13\frac{1}{64}$	3	< 9	18
F-XV	67%	slow	19	$13\frac{1}{64}$	5	<36	>150
Control	67%	10 sec.	24	$13\frac{13}{64}$	4	<19	33
F-XV	67%	10 sec.	24	$13\frac{13}{64}$	3	70	260
Control	67%	40 sec.	24	$13\frac{13}{64}$	4	12	13
F-XV	67%	40 sec.	24	$13\frac{13}{64}$	2	80	210

The relation between tire deflection, measured by the distance from the center of the wheel to the bearing surface, and tire pressure for the two types of casings is shown in Figure 1, for tires resting on the 4-ft. diameter drum and on a flat surface. It will be seen that the additional deflection induced by the curvature of the drum is equivalent to that which would be obtained by a 5 lbs. per sq. in. reduction in tire pressure, and therefore tends to increase the severity of the cold room test.

Early in the program it was observed in the *x*-ray photographs that the crown of the tube tended to shift forward in the casing in the direction of rotation of the wheel, and that this effect always preceded the incidence of buckling.

The rates of crown shifting in 67 per cent casings at 19 and 24 lbs. per sq. in. pressure are shown in Figure 2 for the various types of acceleration. These results substantiate the conclusions drawn from the data shown in Table IV, and also indicate that to a lesser extent more severe acceleration adversely affects tube performance.

(2) *Rate of temperature rise at tube crown surface.*—It was of interest to determine the duration of low temperature conditions at the tube crown surface

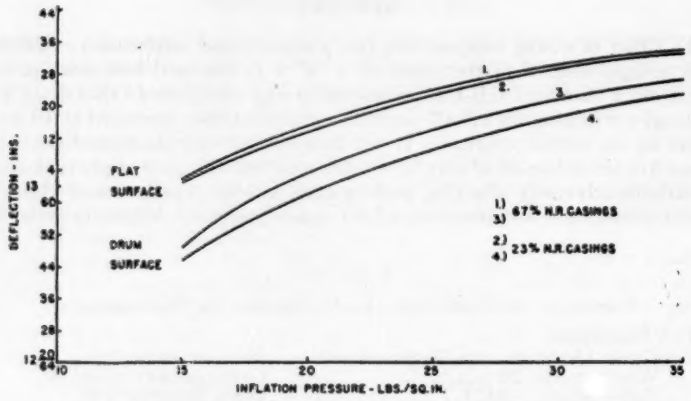

FIG. 1.—Casing deflection vs. inflation pressure (deflection measured from center of wheel hub to surface).

after the start of each cycle. For this purpose a casing was drilled and several thermocouples positioned at the inner crown surface. The tube was mounted in the normal manner and tested at 10-second acceleration, −10° F, and 24 lbs. per sq. in. The rate of temperature rise with respect to tire revolutions is plotted in Figure 3. Previous experience has shown that Butyl-tube performance is satisfactory, provided that the operating temperature is not below zero Fahrenheit for continued periods. Data in Figure 3 indicate that this temperature rises above zero Fahrenheit within ten revolutions (approximately 10 seconds) after the start of the run under the stated test conditions.

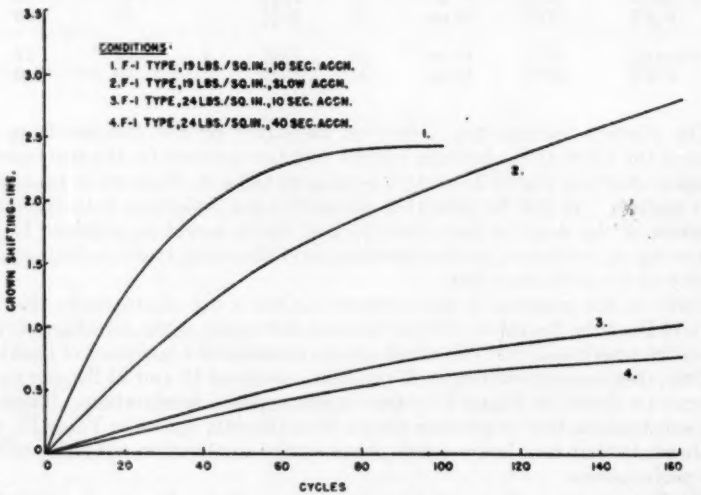
CONDITIONS:
1. F-1 TYPE, 19 LBS./SQ.IN., 10 SEC. ACCN.
2. F-1 TYPE, 19 LBS./SQ.IN., SLOW ACCN.
3. F-1 TYPE, 24 LBS./SQ.IN., 10 SEC. ACCN.
4. F-1 TYPE, 24 LBS./SQ.IN., 40 SEC. ACCN.
CROWN SHIFTING - INS.
CYCLES

FIG. 2.—Effect of acceleration and inflation pressure on the rate of crown shifting in 67 per cent natural rubber casings.

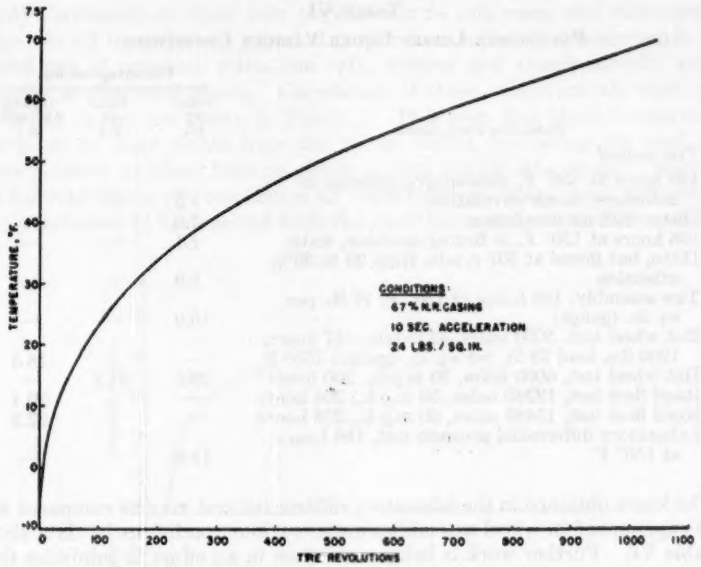

FIG. 3.—Rate of temperature rise at tube-crown surface.

(3) *Effect of plasticizer viscosity on tube performance and plasticizer losses.*—In Table V is shown the performance of tubes containing 25 parts oils of various viscosities and the losses of these oils in the volatility test and the differential pressure test. It will be seen that losses measured by the latter procedure are considerably greater than can be accounted for by volatilization and that such losses are appreciable even with oils so viscous that they make no contribution to low temperature performance.

TABLE V

EFFECT OF PLASTICIZER VISCOSITY ON INNER TUBE PERFORMANCE

Test conditions:

Acceleration: 10 seconds
Cycle: 15-minute run 30-minute soak
Tire loading: 915 lbs.
Tire and tube size: 600 > 16
Tire type: 67% natural rubber
Wind velocity: 20 m.p.h.
Temperature: −10° F
Running speed: 38.8 m.p.h.
Miles per cycle: 9.6
Cycles per day: about 30
Drum diameter: 4 ft.
Mounting procedure: talc

Inner tube formulation	Plasticizer	Viscosity at 80° F (centipoises)	No. of tests	Number of cycles to incidence of buckle	Number of cycles to chafing failure	% Plasticizer loss Volatility test	% Plasticizer loss Differential pressure test
GR-I 15	None	—	9	<22	22	—	—
F-I	Indopol H-300	51,000	4	<17	23	1.1	4.2
F-I	Dutrex-6	21,000	4	<12	17	0.51	10.0
F-I	Circosol-2XH	1,390	4	<16	20	1.4	11.6
F-I	DB-61	177	4	<24	74	2.0	12.6
F-I	Forum-56	158	4	68	155	2.5	13.5
F-I	Frigol-50	104	4	<23	80	3.5	13.8
F-I	Polar-45	76	3	68	260	5.1	15.9
F-I	Barosa-43	44	2	—	>550	—	15.9

TABLE VI

PLASTICIZER LOSSES UNDER VARIOUS CONDITIONS

Plasticizer Formulation	Percentage oil lost		
	Polar 45 F-I	Polar 45 F-I	Galena CC-10W F-I
Test method			
168 hours at 150° F, atmospheric pressure in autoclave, no air circulation	1.5	—	—
Ditto, with air circulation	7.0	—	—
168 hours at 150° F, in flexing machine, static	1.1	—	—
Ditto, but flexed at 307 c/min. from 20 to 30% extension	5.9	—	—
Tire assembly, 168 hours at 150° F, 27 lb. per sq. in. (gauge)	10.0	—	—
Hot wheel test, 5000 miles, 30 m.p.h., 167 hours, 1200 lbs. load 28 lb. per sq. in. (gauge) 155° F	—	—	18.5
Hot wheel test, 6000 miles, 30 m.p.h., 200 hours	20.5	24.2	—
Road fleet test, 12240 miles, 50 m.p.h., 204 hours	—	—	20.4
Road fleet test, 15483 miles, 60 m.p.h., 258 hours	—	—	22.2
Laboratory differential pressure test, 168 hours at 150° F	15.9	—	—

The losses obtained in the laboratory differential test may be compared with those experienced in wheel assemblies under various conditions by data shown in Table VI. Further work is being carried on in an effort to minimize these plasticizer losses and assess their effect on low temperature tube performance.

(4) *Internal lubrication.*—The use of a lubricant applied inside the inner tube to prevent chafing occurring in tubes which have become buckled was first investigated[6] in 1945 by members of the Tire Technical Committee, and a further limited investigation was carried out recently. According to limited data summarized in Table VII, internal application of glycol increases the life of a standard GR-I 15 tube eight-fold at −10° F and four-fold at −20° F, without appreciably delaying the onset of buckling. With *F*-1 type tubes internal application of glycol, methanol, or castor oil leads to a three-fold increase in the cycles required to produce buckling at −10° F, and gives extensive life before failure even at −20° F.

TABLE VII

EFFECT OF INTERNAL LUBRICANTS ON TUBE PERFORMANCE

Type of tube	Lubrication	Temperature (° F)	No. of tests	No. of cycles to incidence of buckle	No. of cycles to chafing failure
GR-I 15 (control)	None	−10	3	18	33
GR-I 15 (control)	200 grams glycol	−10	1	12	270
GR-I 15 (control)	50 grams glycol	−20	1	27	147
F-I	None	−10	3	68	260
F-I	200 grams glycol	−10	1	204	—
		−20		—	357 (total)
F-I	200 grams methanol	−10	1	237	—
		−20		—	422 (total)
F-I	200 grams castor oil	−10	1	201	—
		−20	–	—	>410

(5) *Correlation of inner tube performance in cold room and laboratory test data.*—On all formulations reported in previous sections, measurements were carried out of rebound, retraction rate, viscous and elastic moduli, and oil viscosity as described above. Correlation of these measurements with cycles to chafing failure are shown in Figure 4. It is seen that there is appreciable divergence of some points from the curves drawn, indicating the need for a higher number of wheel tests to obtain a good statistical average. However, it is believed that a combination of all these tests provides a good indication of the performance to be expected from the inner tubes under specified conditions.

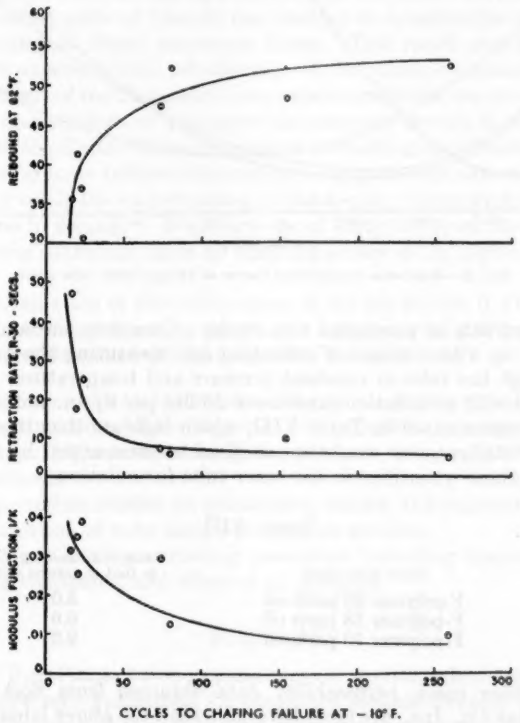

FIG. 4.—Correlation of laboratory tests with cold-room performance of Butyl inner tubes.

A final indication of the degree of improvement in low temperature properties of Butyl attainable by use of plasticizers is shown in Figure 5 by the variation in percentage rebound with temperature of natural rubber, GR-I 50 and plasticized GR-I R-13 formulations, in a manner similar to that previously described by Mullins[4]. It is seen that the temperature corresponding to minimum resilience has been lowered from +5° to −10° F by the use of 25 parts plasticizer, but that the percentage rebound itself has not been appreciably increased.

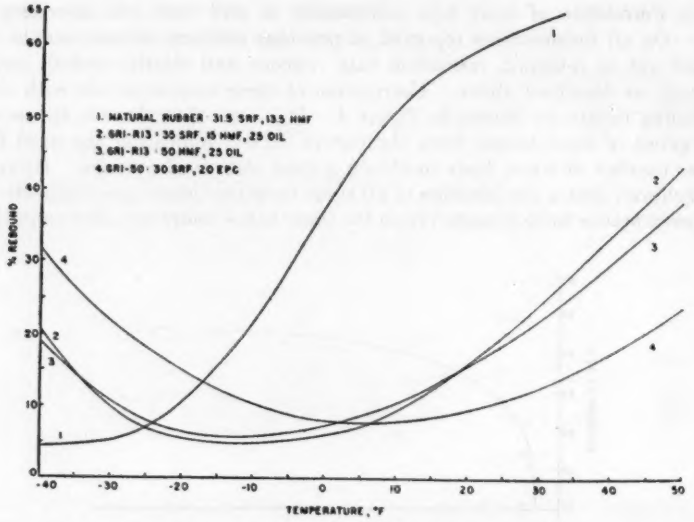
1. NATURAL RUBBER 31.5 SRF, 13.5 HMF
2. GRI-R13 + 35 SRF, 15 HMF, 25 OIL
3. GRI-R13 + 50 HMF, 25 OIL
4. GRI-50 + 30 SRF, 20 EPC
% REBOUND
TEMPERATURE, °F

FIG. 5.—Resilience-temperature curves of various inner tube stocks.

(6) *Permeability of plasticized tube stocks.*—Complete tire and tube assemblies were set up with a means of collecting and measuring the quantity of air passed through the tube at constant pressure and temperature. Preliminary data obtained with an inflation pressure of 50 lbs. per sq. in. and a temperature of 82° F are summarized in Table VIII, which indicate that the air retention property of Butyl polymer would be sacrificed to some extent by incorporating plasticizer in these quantities in the inner tube formulation.

TABLE VIII

Inner tube stock	Ratio of air-holding ability to that of natural rubber
F-polymer 26 parts oil	3.0
F-polymer 18 parts oil	6.6
F-polymer 10 parts oil	9.6

On the other hand, permeability data obtained from fleet tests run in Texas by Enjay Co., Inc., are more favorable than the above laboratory results. A standard air-holding procedure was followed, wherein the tubes were initially inflated to 28 lbs. pressure at room temperature, and no air was added until the pressure had dropped below 22 lbs. at room temperature on any one tube of the test car, at which time all four tubes were reinflated to the original 28 lbs. pressure. The results are indicated below.

Identification	Mileage at 60 m.p.h.	Total air (lb. per sq. in.)
Natural rubber	32,630	29.2
Conventional GR-I	32,916	5.3
R-13 + 25 parts Galena CC-10W	32,916	8.3
R-13 + 25 parts Polar-45	32,916	5.0

DISCUSSION

Coöperation between the Canadian rubber industry and the Standard Oil Development Co. and Polymer Corporation on the development of Butyl inner tubes for low-temperature service was extended in 1947 by several companies to large-scale production of passenger car tubes, using plasticized GR-I R-13 formulations. Many of these went into service in Canada during the exceptionally severe winter of 1947–48. A complete evaluation of their performance cannot be made, however, until the winter of 1948–49 after exposure to summer driving conditions.

Meantime, however, increasing awareness on the part of the public operating cars in the coldest parts of Canada has resulted in considerable increase in the returns of standard Butyl passenger tubes. This result and the additional adverse effect expected from introduction of the wider low-pressure type tires influenced several of the Canadian companies to make the use of natural rubber optional for manufacture of passenger car tubes for service in Canada. This conforms with the United States practice of permitting use of natural rubber in the allocation for inner tubes on the understanding that the natural rubber tubes will be sold for use in the coldest section of the country where winter temperature resemble those in Canada. Voluntary use of Butyl for truck and bus tubes in Canada is being continued, since no buckling occurs at the higher tire pressures used.

Pending evaluation of the performance of the plasticized R-13 type tubes in actual service, a comprehensive program is being carried out by the Polymer Corporation and Standard Oil Development Co. as follows:

(1) Modification of Butyl to improve intrinsic low-temperature performance.
(2) Achievement of a higher degree of vulcanization by a more unsaturated. polymer, higher vulcanizing temperature, alternative vulcanization procedures.
(3) Compounding studies on plasticizers, blacks, and pigment dispersion.
(4) Modification of tube design to equalize stresses.
(5) Variations in tube mounting procedure, including internal lubricants, casing treatment, and effect of air pressure.

SUMMARY

Standard Butyl inner tubes in passenger car service, when operated at temperatures below zero Fahrenheit for continued periods, develop buckles which may eventually cause chafing failures. This effect is believed to be due to increase in the viscous modulus compared with the elastic modulus of Butyl at low temperatures. The effect on performance of such factors as tire pressure, casing composition, and acceleration have been investigated, improved formulations consisting of highly plasticized, high-molecular-weight Butyl have been studied and correlations established between tube performance and physical characteristics, such as rebound, rate of retraction, modulus function, and oil viscosity. While commercial evaluation of such formulations is proceeding, other approaches are being studied by Canadian and United States groups, particularly involving polymers which may be brought to a more complete state of vulcanization.

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THE INTERPRETATION OF PLASTICITY MEASUREMENTS *

J. R. Scott and R. W. Whorlow

INTRODUCTION

Because of the great variety of socalled plastometers introduced for testing unvulcanized rubber, a socalled plasticity result may involve any one (or combination) of several distinct fundamental flow properties of the rubber. This paper attempts, by considering these properties, to indicate how far the commoner types of plastometer would be expected to give results which correlate with each other and with processing properties.

To characterize the rheological properties of rubber, it is necessary to determine its rate of flow under given conditions of stress, temperature, and time of application of stress, the influence of changes in any of these variables on the rate of flow, and the elastic recovery on removal of the applied stress. Recovery, although important in technical practice, will not be fully discussed here.

PLASTOMETERS GIVING FUNDAMENTAL RHEOLOGICAL PROPERTIES

The only existing plastometers which measure a rheological property under well defined conditions, variable at will, are of the rotation type. The best known example, the Mooney shearing disc plastometer[1], measures the stress as a function of time and temperature required to shear the rubber; it thus shows the degree of structure breakdown during a test, and whether it is permanent or nonpermanent (thixotropic). A modification (shearing-cone plastometer) using a biconical rotor and variable-speed drive[2] shears the rubber at a uniform rate throughout its volume (unlike the Mooney, where the rate is not uniform), and measures the stress set up at various uniform shear rates. The Mooney concentric-cylinder rubber rheometer[3] also gives an approximately uniform shear stress, at various rates of shear, the rubber being confined by rubber-faced rings between the cylinders. Hamm[4] has published numerous results from an instrument modelled on that of Mooney.

In using these instruments several factors must be borne in mind.

Temperature rise.—At high shear rates the work done in shearing, the rubber may raise its temperature considerably. For natural rubber sheared between infinite parallel plane surfaces 0.2 cm. apart, assuming that flow is laminar and heat is readily dissipated from the surfaces:

$$T = 3 \cdot 7.10^{-7} \, S \frac{d\sigma}{dt} \text{ degrees } C \qquad (1)$$

where T is the maximum temperature rise within the rubber, S the shear stress in dynes per sq. cm, and $d\sigma/dt$ the rate of strain in radians per seconds.

Research Association of British Rubber Manufacturers, Croydon, England

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Slip.—In all the instruments so far mentioned, the metal surfaces in contact with the rubber are roughened to minimize slip and, except in Hamm's work, the rubber is maintained under hydrostatic pressure at high rates of shear, where slip is most likely. Results with the shearing-cone plastometer, showing only a small effect on varying the hydrostatic pressure, and some results by Mooney[5] show that slip is not important. To reduce friction, Hamm[4] did not keep the rubber under pressure, and found evidence of slip, but this was not serious at the moderate shear rates used, and should be less at lower rates or with the rubber under pressure.

Thixotropy.—Unvulcanized rubbers may exhibit thixotropy, as shown by the variation of the torque with time in the shearing-cone plastometer (Figure 1). For any comparison of rubbers, they should be in the same state of thixotropic breakdown, and this may present difficulties in view of the different rates of this breakdown in different rubbers (*cf.* Figure 1).

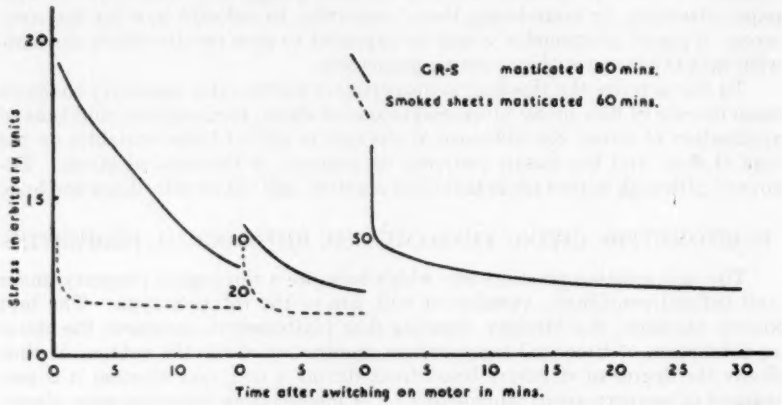

FIG. 1.—Variation of stress with time at constant rate of strain (1 sec.$^{-1}$). The motor was switched off in the course of the experiment for the times shown (in minutes), to illustrate the thixotropic nature of the stress variations.

STRESS/SHEAR-RATE RELATIONSHIP FORM ROTATION INSTRUMENTS

Typical results are plotted logarithmically in Figure 2.

The curve A from the concentric-cylinder rheometer[3] is the only complete curve, down to very low shear rates, published by Mooney. The dotted lines, indicating the temperature rise (from Equation 1) under various stresses and rates of strain, cast doubt on the validity of the highest points on curve A. Another curve B given in Mooney's paper seems meaningless in view of the large temperature rise involved. Mooney's observation that a constant shear rate was not attained at the highest stresses, as the rotor could turn through only two revolutions, suggests that temperature equilibrium was not reached owing to the time taken to heat the rubber.

Curve C shows the type of result obtained by Hamm[4] under conditions generally similar to those of Mooney. Although this appears to confirm Mooney's result, all curves given by Mooney are curved at high shear rates and linear at lower rates, whereas those of Hamm which show curvature tend to become linear at higher shear rates.

For the lower part of Curve D, from the shearing-cone plastometer[2], the rotor was driven by a pulley and weights. The rubber was under a small hydrostatic pressure (about 15 kg per sq. cm.), since, although measurements at the highest shear rates were unaffected by an increase in pressure to 70 kg. per sq. cm. (indicating slip was not important), at lower shear rates this higher pressure apparently forced the rotor hard against the stator and introduced friction, which is important only at these lower shear rates. For all points on this curve the ratio of rate of stress to rate of strain had reached a steady value, except possibly at the highest rate of shear, and the stress has been corrected for residual friction.

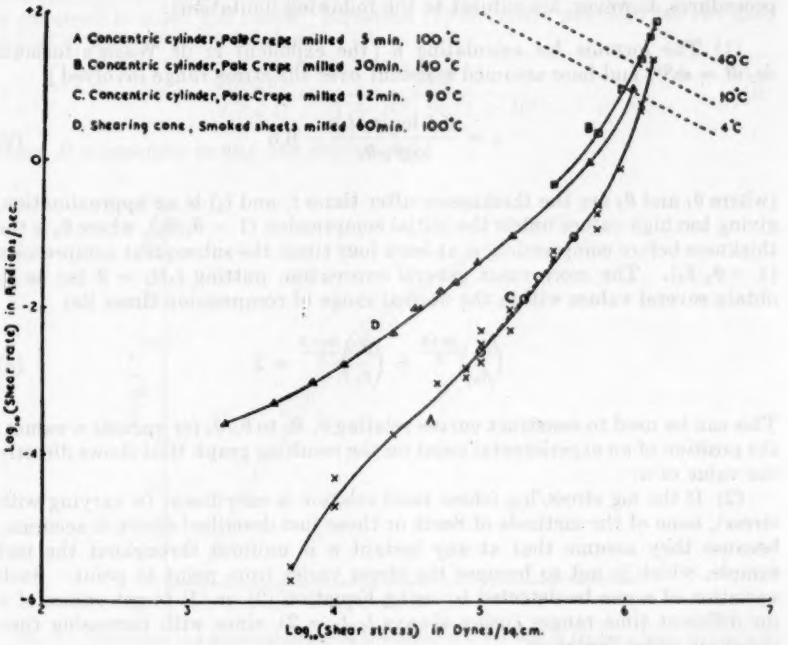

FIG. 2.—Variation of strain rate with stress for raw rubber.

It is not possible to tell whether the downward trend of Mooney's curve A is due to friction or a yield stress for the rubber, but the former seems probable in view of Mooney's references[3] to "small but observable friction" in spite of a reduction of the pressure on the confining rings.

These results show that, for uncompounded rubber at 90° to 100° C, the log (shear stress)/log (shear rate) plot is straight or slightly curved at shear rates less than about 0.1 sec.$^{-1}$, but may be markedly convex to the log stress axis at higher rates. Curve D, if replotted on nonlogarithmic scales, shows that well masticated natural rubber at 100° C exhibits Newtonian flow at very low stresses. Any yield stress appears negligible compared with stresses met in processing; the yield value indicated by earlier parallel-plate compression tests[6] is thus not definitely confirmed. These conclusions refer to unmixed rubber;

mixed stocks, particularly those containing reinforcing fillers, have shown more definite evidence of a yield value[6], although in Hamm's work on such stocks, over the limited range of shear rates considered, the curvature was in the opposite sense to that expected for a material with a yield value.

STRESS/SHEAR-RATE RELATIONSHIP FROM COMPRESSION PLASTOMETERS

Methods are available for determining fundamental constants from parallel-plate compression data[7], but as these are too cumbersome for general use, an attempt has been made to devise quicker and simpler procedures[8]. These procedures, however, are subject to the following limitations:

(1) The formula for calculating n [the exponent in de Waele's formula $d\sigma/dt = \phi S^n$, and here assumed constant over the stress range involved]:

$$n = \frac{0.4 \log(t_2/t_1)}{\log\theta_1/\theta_2} - 0.6 \qquad (2)$$

(where θ_1 and θ_2 are the thicknesses after times t_1 and t_2) is an approximation, giving too high values unless the initial compression $(1 - \theta_1/\theta_0)$, where θ_0 is the thickness before compression, is at least four times the subsequent compression $(1 - \theta_2/\theta_1)$. The more exact general expression, putting $t_2/t_1 = 2$ (so as to obtain several values within the normal range of compression times)is:

$$\left(\frac{\theta_1}{\theta_0}\right)^{\frac{5n+3}{2}} + \left(\frac{\theta_1}{\theta_2}\right)^{\frac{5n+3}{2}} = 2 \qquad (3)$$

This can be used to construct curves relating θ_1/θ_0 to θ_1/θ_2 for various n values; the position of an experimental point on the resulting graph thus shows directly the value of n.

(2) If the log stress/log (shear rate) relation is curvilinear (n varying with stress), none of the methods of Scott or those just described above is accurate, because they assume that at any instant n is uniform throughout the test sample, which is not so because the stress varies from point to point. Such variation of n can be detected by using Equation (2) or (3) to get values of n for different time ranges (using always $t_2/t_1 = 2$), since with increasing time the shear stress decreases.

(3) Apparent variations in n, however, may arise from other causes: (*a*) if the material possesses a yield value, n appears to increase with increasing compression time; (*b*) a decrease in n from an initially high value to an approximately constant lower value can be caused by an initial high-elastic deformation superposed on viscous deformation; this leads to spuriously high n values, by either Equation (2) or (3), especially when θ_1 and θ_2 are not very different from θ_0.

It is clear that unless application of Equation (2) or (3) gives values of n substantially independent of the compression time, the results have only qualitative significance, and should not be used to deduce the stress/shear-rate relation by the method of Scott[8]. Moreover, from the discussion above, it is clearly important to arrange test conditions so that the compressed thickness is much smaller than the initial thickness.

APPLICATION OF THE NUTTING EQUATION TO COMPRESSION PLASTOMETER DATA

As attempts have been made[9] to interpret parallel-plate plastometer data by the Nutting equation:

$$\psi = S^{\beta}\sigma^{-1}t^{k} \tag{4}$$

where S is the stress, σ the strain (here $ln\ \theta_0/\theta$), t the time, and ψ, β, and k are constants, *i.e.*, using $\frac{d(\log \sigma)}{d(\log t)}$ as a measure of k. It is important to realize the limitations of this procedure. If, as in the normal Williams test, the rubber does not slip over the confining surfaces, and the strain is large, the value of k so obtained is much too small. Equation (7) of Scott[6], modified for the case of $k \neq 1$, leads to the following:

$$\frac{d(\log \sigma)}{d(\log t)} = \frac{kBt^{k}}{(1 + Bt^{k})\ ln\ (1 + Bt^{k})} \tag{5}$$

where B is constant in any one experiment.

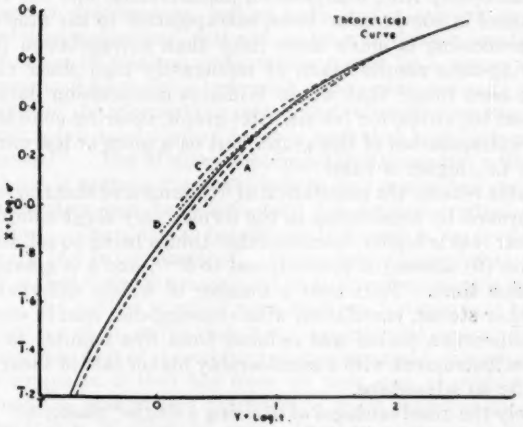

FIG. 3.—Theoretical and experimental curves illustrating that the form of the log σ/log t relation is independent of the material tested (provided $k = 1$) and is nonlinear. $X = \log_{10}(5n + 3)/2$; Y is a function of n, c, θ_0, volume of specimen, and compressive force.

As t increases from 0 to ∞, $d \log \sigma/d \log t$ decreases from k to 0, and thus in general does not equal k. This has been confirmed by experiments on materials (Aroclor mixtures) known to have $k = 1$ for small strains (see Figure 3). The same conclusion is true for compression plastometers in which the load increases proportionately to the cross-sectional area of the specimen.

PLASTOMETERS FOR FACTORY CONTROL

As extrusion plastometers do not really measure plasticity[10], so that no close correlation with rheological properties is to be expected, they will not be considered further.

The only rotation instrument used for control purposes, the Mooney shearing-disc viscometer[1], operates at a mean shear rate (about 0.8 sec.$^{-1}$) well below

those involved in processing. Curves A and D in Figure 2 show that measurements at such a low shear rate may give a misleading impression of the difference between two rubbers. It would, therefore, be an advantage to have Mooney viscosity readings at other speeds, so that behavior at high shear rates could be more accurately estimated. This defect is even more serious in the compression plastometers; thus, in the Williams type the mean shear rate, given by:

$$\frac{A V^{\frac{1}{2}}}{\theta^{5/2}} \cdot \frac{d\theta}{dt} \text{ sec.}^{-1} \qquad (6)$$

(where A is a constant, approx. 0.6; V = volume of specimen, cc.; θ = thickness of specimen, cm.), never exceeds about 0.1 sec^{-1}. It is possible, by assuming that the logarithmic stress/strain-rate relation is linear, to calculate, from compression plastometer data, this relation over the range of shear rates given by the test[11], this gives a better idea of the behavior of the rubber than the usual single Williams plasticity or Defo number. However, in view of the limitations of this procedure, especially arising from the existence of curvilinear log stress/log (strain rate) relationships (see discussion above on the stress/shear rate relationship from compression plastometers) and the very low rates of shear obtained in compression tests, extrapolation to the much higher rates involved in processing is much more risky than extrapolation from shearing disc or shearing-cone results taken at moderately high shear rates. It has, indeed, often been found that where Williams compression data gave a substantially linear log stress/log (strain rate) graph, shearing-cone test results did not lie on an extrapolation of this graph, but on a more or less curved line with greater slope, *i.e.*, higher n value.

For the same reason, the correlation of Williams and shearing-disc plasticity results is improved by considering in the former very short compression times, where the shear rate is higher, because other things being equal, the mean shear rate (Equation (6) above,) is proportional to $\theta^{5n/2}$, and θ is greater the shorter the compression time. Thus over a number of widely different natural and synthetic rubber stocks, correlation with shearing-disc results was much closer when the compression period was reduced from five minutes to six seconds[12]. A compression instrument with a considerably higher rate of shear than existing types would be an advantage.

Fortunately the disadvantages of utilizing a single "plasticity" figure are not in practice as serious as might at first appear. In general, any likely source of variation between repeat batches will alter this "plasticity" figure, and since fairly wide tolerances are usually allowable in processing, the test can provide reasonably adequate control. However, to consider a particular example, a simultaneous decrease in both mastication time and filler content, which would markedly affect processing, might leave the Williams plasticity figure unchanged, and the same effect could occur if the plasticizing treatment were changed[13], but a plasticity test using a high shear rate, closer to that in processing, would be more likely to reveal the difference.

This may explain the apparent superiority of the shearing-disc viscometer in controlling mastication of GR-S, since the shape of the stress/shear rate curve depends markedly on the way it is plasticized. For example, hot and cold Banbury mastications give very differently shaped curves even though (say) the Williams five-minute thickness figure is the same[14]. These examples show that the usefulness, for control purposes, of a plastometer that gives a single reading applies only to a stock for which control limits have been established,

and that these limits cannot be carried over to a different mix or even to stocks plasticized or mixed differently.

REQUIREMENTS OF RESEARCH AND CONTROL PLASTOMETERS

The foregoing indicates a need for two types of apparatus: (1) for research on the fundamental properties of rubber stocks or evaluation of the processing qualities of a new stock; (2) for factory control. To conclude this paper, the available instruments in each group are briefly reviewed in relation to these requirements.

The basic requirements of the first type are accuracy, the measurement of a definite property under well defined conditions, and a wide range of all possible variables, changing independently. Both shearing-cone and concentric-cylinder types are reasonably satisfactory, except in not giving shear rates as high as those of practical interest. They have been, or could be, adapted to measure elastic recovery[15] or the related property of stress relaxation at constant strain[16] although, in measuring the former, difficulties may arise from friction and the high moment of inertia of the moving parts. It seems desirable, moreover, to measure recovery after very rapid deformation such as occurs in a calender or extruder. Such a deformation, lasting only half a second, is given in the Williams pendulum apparatus[17] but not under well defined conditions. A desirable modification of rotation instruments would be a means of applying a very rapid motion of large amplitude with subsequent recovery measurement.

In apparatus of the second type, speed and reliability are required, but the variability within the usual factory batch is such that high instrumental accuracy is not essential[18]. The Mooney shearing-disc viscometer, with its relatively high rate of shear, is perhaps the least likely to give misleading results, but compression plastometers can be satisfactory for routine control of nominally identical batches. The original parallel-plate type[19] is as good as any, provided a recovery test is not required. It has been claimed that modifications in which one[20] or both[21] plates are reduced to an area comparable with the initial cross-section of the rubber samples give readings independent of the sample volume, but this is not so, as the ring of surplus material surrounding the plates restricts the outward flow of the rubber being compressed; the second advantage of these smaller plates is that the force on unit area of rubber does not fall rapidly, so that the compressed thickness is more sensitive to differences in plasticity, but this is of doubtful value, because accuracy is limited by the variation between nominally identical specimens.

The Defometer[18] differs from other compression instruments in that the compression time and distance are fixed, and the load is varied. The main advantage of this is that recovery for different samples is measured after a similar strain, but for control work on nominally identical batches this may not be important because plasticity and recovery are then fairly closely related[22].

The time taken to prepare the constant-volume specimens needed with all types of compression apparatus can be reduced by using a rotary cutter to produce cylindrical specimens.

By such automatic cutters, and refinements in measuring technique, the time taken to prepare a specimen and make a measurement, including recovery, has been reduced considerably, but the problem of reducing the time taken to bring samples to the test temperature before measurement has apparently been tackled in only one case. The important factor is to reduce specimen thickness, and in the Hoekstra rapid stream plastometer[23] the initial thickness is only 1 mm., allowing a preheating time of 15 seconds.

The design of an instrument combining as many as possible of the good points of existing plastometers—simple, rapid, fairly accurate, and able to measure recovery—cannot be envisaged satisfactorily until more is known about the reasons for the advantages claimed for the many types, but further fundamental study of rheological behavior in instruments and processing machines will lead to more satisfactory control than in the past, resulting in easier processing and improved quality of products.

SUMMARY

After consideration of the various factors whose influence must be included in any complete assessment of the fundamental flow properties of uncompounded raw rubber, a comparison is made of results from various instruments. It is shown that a plot of log (shear stress) against log (strain rate) is straight or slightly curved at low shear rates, but may be markedly convex to the log stress axis at higher rates.

Reference is made to the limitations of the methods of Scott for the interpretation of the results of parallel-plate compression tests; attempts to apply the Nutting equation to the large strains in the usual compression tests with rubber are shown theoretically, and by experiments on materials of known characteristics, to be invalid.

Consideration of the instruments available for factory control purposes shows that the one figure obtained from conventional tests is inadequate for the evaluation of a new mix or even a new plasticizing or mixing technique, and alternative procedures are considered; for the control of nominally identical batches a single figure may be adequate.

Finally, the essential requirements for research and control instruments are compared, and available instruments in each group surveyed in the light of the earlier discussion.

ACKNOWLEDGMENT

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THE CONTROL OF UNDESIRABLE VISCOSITY INCREASES IN LATEX COMPOUNDS*

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INTRODUCTION

In controlling the properties and behavior of rubber latex as a disperse system, *i.e.*, before coagulation, frequent reference is made to the use of anionic and cationic surface-active agents. It has more recently become well known that a third group of surface-active agents possesses useful and indeed valuable properties, *viz.*, the nonionogenic surface-active agents[1]. These, unlike the two ionogenic groups first mentioned, are substances which owe little or none of their efficacy to any change they may effect in the sign or magnitude of the electric charge carried by colloidal particles dispersed in the aqueou s system to which they are added. The present writer has recently published a generalized and simplified account of these and related questions of the mechanization of latex stabilization and stabilizer action[2].

For example, the writer had available supplies of a water-soluble substance of this type consisting of a fatty alcohol-ethylene oxide condensate and hereinafter referred to as nonionogenic stabilizer A (the material actually used was Vulcastab-LW of Imperial Chemical Industries, Ltd.), which was known to be effective as a deflocculating agent and protective colloid for disperse systems, being strongly adsorbed on the dispersed phase and owing its stabilizing power to the solvation of the adsorbed layer, this solvation being relatively unaffected (1) by changes in the *p*H value of the dispersing phase, (2) by the presence of calcium, magnesium, and other multivalent metal ions. It was thought desirable to evaluate this substance as a stabilizer for use in latex technology, and the remainder of this paper is concerned with a brief report of such of the resulting observations as are judged to be of practical value to latex technologists. Stabilizer-A possesses properties technologically similar to Emulphor-O (I.G.), which is stated to be a condensate of ethylene oxide and oleyl alcohol[3]. The generalized formula of compounds of this type, R being the fatty alcohol radical (and hydrophobic head of the molecule) is:

$$R—O—C_2H_4—O—C_2H_4—O—C_2H_4—O\ldots\ldots C_2H_4OH.$$

In a compounding-stirring test similar in details to one already described[4], it was observed that the nonionogenic stabilizer A was, on an active weight basis, 50 per cent more effective than a well known anionic stabilizer[5] consisting of the sodium salt of oleyl *p*-anisidine sulfonic acid and hereinafter referred to as anionic stabilizer B. Since the solubility of stabilizer A was known to be relatively unaffected by water-soluble salts of multivalent metals, it was anticipated that it would possess the virtue of protecting latex compounds against the well known zinc oxide thickening effect[6] (for an earlier discussion of this

* Reprinted from the *Proceedings of the Second Rubber Technology Conference* (London), 1948, pages 312–318.

effect and its mechanism see work by Jordan[7]) and against multivalent ion destabilizing effects in general.

Experimental investigation was therefore undertaken, with successful results.

CONCLUSIONS

It was shown that the use of nonionogenic stabilizer A made possible successful control of zinc oxide thickening in simple latex-zinc oxide compounds and of the thickening that develops when latex is allowed to stand, fully compounded for vulcanization, using active accelerators. At the same time, the useful properties of the accelerators studied, *viz.*, zinc diethyldithiocarbamate, zinc dibutyldithiocarbamate, and the well known combination of sodium isopropylxanthate with diethylammonium diethyldithiocarbamate, were not prejudiced by the stabilizer, which tended to have a beneficial effect. Finally, the storage instability of a well established heat-sensitive latex compound was favorably influenced by the stabilizer. These useful effects were secured by the use of quantities of the nonionogenic stabilizer A that are insufficient to interfere with the use of standard coagulants, *e.g.*, in the production of dipped goods. Further, it was shown that the effect of this stabilizer on the water absorption of the latex rubber film is not large and is, in any case, destroyed by heat treatment of the degree and duration used in a normal heat cure. The point is made that for all the above useful purposes, the well known anionic stabilizer B proves of little or no help. It is evident that in nonionogenic stabilizer A, the latex technologist has acquired a new and most useful addition to his auxiliary product tool chest.

ZINC OXIDE THICKENING

A booty-latex (60 per cent rubber content, centrifuge-concentrated, ammonia-preserved, captured after reoccupation of Malaya) on compounding with 1.5 per cent of dispersed zinc oxide (calculated on the rubber content) coagulated completely in 12 hours in the absence of any stabilizer and in 24 hours in the presence of 1 per cent of anionic stabilizer B. In the presence of 1 per cent of nonionogenic stabilizer A, the viscosity of the above simple latex-zinc oxide compound, as measured by the outflow time in a simple type of jet viscometer[8], had increased by only 37 per cent of its original value after 30 days' standing at room temperature.

In presenting this communication, it is felt desirable in the interests of clarity to give all the experimental data in the above simplified form rather than in the form of time-viscosity graphs or as the original and very complete tables of data, from which only selections will be given to illustrate the points to be made. The latex referred to throughout this communication is, similarly, an ammonia-preserved and centrifuge-concentrated normal commercial product of 60 per cent rubber content and of good postwar commercial quality.

This good quality latex was similarly compounded with 1.5 per cent zinc oxide. Here, the zinc oxide stability was initially much more satisfactory, the unstabilized mix increasing in viscosity by 25 per cent after standing 30 days at room temperature and by 170 per cent after 90 days (*cf.* complete coagulation in 12 hours where booty latex was used). Here, in the presence of 1 per cent of anionic stabilizer B, viscosity increased to about 200 per cent of the original value in 14 days but 1 per cent of nonionogenic stabilizer A gave such protection that the viscosity increase after 30 days' standing was only 13.5 per cent and after 90 days was 50 per cent (*cf.* 170 per cent without stabilizer).

ACCELERATOR THICKENING IN LATEX MIXES

Attention was directed to the well known thickening effect experienced when latex containing sulfur and zinc oxide is compounded with active ultra-accelerators, particularly those able to bring about room temperature vulcanization. The general compounding formula utilized, except where otherwise stated, was:

Rubber (in latex form)	100
Dispersed sulfur	1
Dispersed zinc oxide	1.5
Total accelerator	1

Dispersions of sulfur, zinc oxide, and water-insoluble accelerators were prepared with the assistance as dispersing agent of a naphthalene formaldehyde sulfonate[9].

ZINC DIETHYLDITHIOCARBAMATE

Using the well known heat-vulcanizing accelerator zinc diethyldithiocarbamate (ZDC), it was observed that, in the absence of a stabilizer, after 17 days at room temperature the mix was so much more viscous than when freshly prepared (greater than 200 per cent) that a measurement was impracticable, whereas after standing for a similar time, that portion of the mix protected with 1 per cent of anionic stabilizer B was 41 per cent more viscous than originally, and the corresponding value with 1 per cent of nonionogenic stabilizer A was only 6 per cent. To illustrate how little of this latter stabilizer can be effective, results may be quoted for a second latex fully compounded with zinc diethyldithiocarbamate, where the control value after 30 days' standing was a 60 per cent increase in viscosity and only 0.25 per cent of nonionogenic stabilizer A showed, in contrast, a viscosity increase of as little as 13 percent. Complementary work was also carried out to elucidate any effect of nonionogenic stabilizer A on the vulcanizing properties of the accelerator zinc diethyldithiocarbamate. No effect was observed on tendency to fluid prevulcanization. It is well known[10] that zinc diethyldithiocarbamate is activated as an accelerator of vulcanization when the latex mix (as is commonly the case) contains ammonia and is allowed to stand for some hours before deposits of latex rubber are isolated, dried, and vulcanized. When ammoniated latex mixes are allowed this full period of maturation in the presence of nonionogenic stabilizer A or in the presence of anionic stabilizer B, the effect of these agents on the speed of subsequent dry heat vulcanization is negligible. These stabilizers both appear to speed up appreciably the speed of maturation, *i.e.*, to obtain the full activation of zinc diethyldithiocarbamate by an ammoniated mix in their presence requires a substantially shorter period of standing than when no stabilizer is included.

ZINC DIBUTYLDITHIOCARBAMATE

Passing now to the somewhat notorious thickening effect of one of the fastest single latex accelerators known, namely zinc dibutyldithiocarbamate (ZNBC), a good quality latex fully compounded and containing this accelerator, after only 10 days' standing, was too thick for the viscometer (more than 400 per cent thicker than when prepared) and the presence of 1 per cent of anionic stabilizer B was of no assistance in correcting this progressive thickening. On the other hand, as little as 0.25 per cent of nonionogenic stabilizer A so retarded the thickening that after 30 days' standing the mix was still fluid, *i.e.*, 130 per cent thicker than when first prepared. A more direct comparison is afforded by the

effect of 1 per cent of A, which, after 10 days' standing, gave a mix showing only a 25 per cent increase in viscosity. As regards the effect of stabilizers A and B on the vulcanization effects associated with ZNBC, it is well known[11] that the speed of this accelerator, as shown in the dry heat vulcanization of latex films or deposits, depends much more on the length of time the ammoniated and compounded mix has been allowed to stand than does ZDC. Here again, stabilizers A and B both have a definite effect in speeding up the rate of this maturation. When full maturation of the mix has been allowed to occur, nonionogenic stabilizer A appears to have no effect on the rate of dry heat vulcanization of films obtained from the latex. Some detailed study has been made of the effect of nonionogenic stabilizer A on the properties of ZNBC for making vulcanized latex simply by storage of the mix at room temperature. Summarizing these results, which embraced independent variations in the content of sulfur, zinc oxide, and accelerator as well as of stabilizer A, it should be pointed out that the tightest fluid vulcanizations were obtained from the mix:

Latex rubber	100
Zinc oxide	1.5
Sulfur	2.0
ZNBC	0.5
Nonionogenic stabilizer A	0.5

after a period of 6 days' standing. The best fluid vulcanization in the absence of zinc oxide came from the mix:

Latex rubber	100
Sulfur	2
ZNBC	1
Nonionogenic stabilizer A	0.5

after standing for 6 days.

It was evident that stabilizer A was activating somewhat the quality of room-temperature fluid vulcanization (as judged by physical test figures), the strongest activation in the absence of zinc oxide occurring with high (1.5 per cent) accelerator and high sulfur (1 to 1.5 per cent). The stabilizer A, nevertheless, appears to have little or no effect on the rate at which a fluid technical vulcanization with ZNBC is reached by standing the mix at room temperature. Under the same conditions, anionic stabilizer B even retards the rate of vulcanization slightly.

Dry room-temperature vulcanization of films from fully matured ZNBC mixes is unaffected in speed by either stabilizer A or B (vulcanization was obtained in 8 days in a room during the winter) and dry room-temperature vulcanization of films from unmatured mixes was obtained under the same conditions, in the absence of stabilizer, in 15 days. Stabilizer B reduced this time to 14 days, showing slight activation, but nonionogenic stabilizer A gave definite activation, giving the vulcanization in 11 days.

The need for distinction between the various types of latex vulcanization and the testing technique used will be found discussed by the writer in previous publications[12].

SODIUM ISOPROPYL XANTHATE–DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE

Interest was finally taken in the control of the latex thickening properties of the well-known SPX/DDCN combination. This is a combination of sodium isopropyl xanthate (SPX) and diethylammonium diethyldithiocarbamate (DDCN). The latex thickening effect of this combination in fully compounded

latex mixes had already been minimized, while retaining reasonable curing activity, by a suitable choice of the accelerator ratio[13] 3 parts of DDCN to 2 of SPX being selected, and in the work now being reported, this ratio was likewise used. Nevertheless, some degree of thickening still occurs on standing fully compounded mixes, and it was sought to control this thickening. A characteristic of this combination, it will be recalled, is that, although the rate of dry room temperature vulcanization of latex films is rapid, the rate of fluid vulcanization of the mix is low, presumably because of the inhibiting effect on the xanthate of the volatile alkali in the latex.

A fully compounded SPX/DDCN mix showed a 60 per cent increase in viscosity on standing for 20 days in the absence of stabilizer, a 19 per cent increase when 1 per cent of stabilizer B was present, and an increase of only 7 per cent in the presence of 1 per cent of nonionogenic stabilizer A. A similar mix made with a different latex sample showed a viscosity increase of 200 per cent after 30 days' standing, but an increase of only 100 per cent in the presence of 0.25 per cent of stabilizer A.

As regards influence on the vulcanizing properties of this combination, it was found that stabilizer A retards the rate of dry room-temperature vulcanization (prolonging the time required by about one-third), but is fortunately without any effect in promoting the characteristically low rate (in the presence of ammonia) of fluid vulcanization.

OTHER METHODS OF THICKENING CONTROL

Mention should here be made of a rather obscure phenomenon[14] which is nevertheless well known to practical latex technologists, *viz.*, the control of storage thickening effects in latex compounds by an increase in the zinc oxide content. Thus, it was observed that, while a particular fully compounded ZDC mix increased in viscosity by 60 per cent on standing for 30 days when only 1.5 per cent of zinc oxide was present, the increase amounted to only 50 per cent when 10 per cent of zinc oxide was used. This is not a striking case, but when the accelerator was ZNBC, the corresponding values were 400 per cent or more and 80 per cent, while with SPX/DDCN they were 200 and 41 per cent. While use of excess of zinc oxide would thus appear to afford a means of control, the method presents practical difficulties and is probably more costly on a material basis than the use of small quantities of stabilizer A. Control of zinc oxide thickening by critical additions of caustic potash as discussed by Jordan[7] and by Wren[6] are not overlooked, neither is the usefulness of deammoniation. The former method involves addition of a material that may prejudice the final quality of the rubber, while the latter removes ammonia on which certain vulcanization accelerator effects depend. Both methods require careful and fairly expert laboratory control, and cannot compare in convenience with the noncritical use of a small amount of stabilizer.

EFFECT ON COAGULANTS

It was argued that too effective a latex stabilizer might well prove a handicap in processing operations when coagulant setting is deliberately used and nonionogenic stabilizer A was suspect from the start on theoretical grounds. Nevertheless, it was shown that mixes containing 0.5 per cent of the stabilizer responded perfectly well to the common ethanol-acetic acid coagulant, though not so well to calcium chloride coagulants used for coating dipping formers. With 0.25 per cent of stabilizer A, a quantity already shown effective in a

number of cases, no trouble was experienced, even with the calcium chloride coagulants.

HEAT-SENSITIVE MIXES

Attention was paid to the use of nonionogenic stabilizer A in heat-sensitive latex systems. This material has a negative solubility curve, and solutions cloud at temperatures of about 85° C. On heating, the solutions show a reversible loss of stabilizing power, so a coagulant already present in the latex and prevented by the stabilizer from affecting the latex at room temperature causes gelation when the mix is heated. Similarly, fluid addenda capable of giving a gel on heating will, with stabilizer A, give heat-sensitive mixes. Suitable grades of methylcellulose are of interest in this connection. An important function of stabilizer A is that it permits neutralization of these mixes with acid during the compounding operation. Sutton[15] found it of value in preparing heat-sensitive latex mixes based on the use of polyvinylmethyl ether. The influence of nonionogenic stabilizer A in a well known heat-sensitive mix was of interest. Ammonium sulfate solution (20 per cent) five parts was added to 1.7 parts of zinc sulfate (heptahydrate) first dissolved in water and treated with dilute ammonia solution until the precipitate first formed was redissolved: the whole mixture was finally made up with water to 27 parts weight and added to the standard mix:

	Parts by weight
Latex rubber	100
Sulfur	1.5
Zinc oxide	1.5
ZDC	1

Such a mix normally gels at room temperature in about 7 days, but 0.25 per cent of nonionogenic stabilizer A enabled it to be kept for 14 days with only a 33 per cent increase in viscosity. Anionic stabilizer B is of no assistance in controlling storage viscosity changes in such a mix. Unfortunately, in this case, the nonionogenic stabilizer A has a definite effect in raising the gelling temperature of the mix from 40° to 60° C.

WATER RESISTANCE OF FILMS

In conclusion, a brief note is added on a matter of great interest to practical latex technologists, *viz.*, the effect of nonionogenic stabilizer A on the water resistance of latex films. This body shows signs of possessing some of the transitory properties so much desired. Thus, uncompounded latex rubber films stored in a perfectly dry atmosphere gained weight on transfer to an atmosphere of 60 per cent relative humidity and in the presence of 5 per cent of stabilizer A picked up more water under these conditions. But it was observed that when the films were heated (for 30 minutes at 100° C) before exposure to the moist atmosphere, the film containing the stabilizer no longer showed any tendency to enhanced water absorption.

SUMMARY

A latex stabilizer of the nonionogenic class, consisting of a fatty alcohol-ethylene oxide condensate, similar in chemical type and technological properties to Emulphor-O (I.G.), is shown to be effective in controlling zinc oxide effect thickening and similar undesirable increases in the viscosity of compounded latex mixes, *e.g.*, in the presence of active accelerators under conditions where

an older and better known stabilizer of the anionic synthetic detergent class is not adequately effective. The proposed stabilizer may be effective in as low an amount as ¼ per cent on the rubber, and the material actually used in the experimental work was Vulcastab-LW.

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LATEX-RECLAIM-CASEIN MIXTURES FOR RUBBER-CORD FABRIC ADHESION *

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Since the introduction of rayon into tire casings, latex-reclaim-casein solutions have been widely used for treating the cord to procure a satisfactory bond between the rayon and the casing rubber which surrounds it. A wide range of compositions is possible, as all three of the main components can be varied at will. The experiments described below were carried out with the object of obtaining information about the effect of variations in the composition of this type of adhesive on the physical properties of the solution, the rayon cord, and the bond between casing rubber and cord. Also variations in the method of cord treatment have been investigated.

MATERIALS

The cord used throughout was 3/1100 denier viscose rayon cord made from prestretched singles. A standard natural rubber casing compound, calendered to the desired thickness and stored between holland cloth, was employed in all the experiments. Commercial grades of latex, dispersed reclaim, casein, and borax were used; the dispersed reclaim possessed a dry solids content of approximately 50 per cent. In each group of experiments a single homogeneous sample of each material was used.

METHODS OF TEST

DIPPING

The solutions were made up by dissolving the borax in hot water (65° C) and gradually adding the casein while stirring mechanically. The stirring was continued for at least fifteen minutes after addition of all the casein; the liquid was then cooled to 30° C and the latex, followed by the dispersed reclaim, added while stirring gently. The adhesives were applied to the cord by passing the latter through a bath at room temperature under slight tension, the time of immersion being about 20 seconds. After issuing from the bath it was passed through a tube heated electrically to about 120° C internal air temperature. Drying of the treated cord was completed by heating for two hours at 120° C, and the cord was then allowed to stand for at least two days in an atmosphere at a temperature of 70° F and 65 per cent relative humidity to regain normal moisture content.

VULCANIZATION

Bars of the rubber compound 15 inches long and $\frac{1}{2} \times \frac{1}{2}$ inch cross-section were vulcanized, each containing 18 lengths of cord equidistantly spaced along the bar and passing through it in a direction parallel to one of its transverse axes. The vulcanization temperature was 298° F, the time 30 minutes. The bars were cut into blocks $\frac{3}{4} \times \frac{1}{2} \times \frac{1}{2}$ inch each, with a cord passing along one of

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the transverse axes. Approximately equal quantities of the cords being compared were introduced into each bar, and half the blocks from each bar corresponding with each type of cord were tested for adhesion; the remaining half were flexed as described below before being submitted to the adhesion test. The experiments were arranged in this way to minimize the effect of variations in the building up and vulcanizing of the bars. A number of bars was vulcanized for each group of experiments, and the adhesion figures given in the tables are each the mean of results from about 30 tests.

ADHESION TEST

For the determination of adhesion, a pull-out test was used in which the bond was destroyed by a shearing force. The block was inserted into a holder, the cord being threaded through a hole in the latter and fixed in the upper jaw of a Scott single-thread tester. The holder itself was attached in place of the lower jaw of the testing machine, which was run at a pulling speed of 12 inches per minute. The load required to overcome the adhesion was recorded autographically. The hole in the holder was made as small as conveniently possible to minimize movement of the rubber during the test. Blocks were always left at least 24 hours between vulcanization and testing.

FLEXING TEST

The blocks were inserted in the Goodrich flexometer with the $\frac{3}{4}$-inch dimension vertical, *i.e.*, cord horizontal. A load of 180 lbs. per sq. in. was applied to the sample, which was flexed at a rate of 1450 cycles per minute with a stroke of 0.25 inch. Under these conditions the temperature at the center of the sample rose to 160° F in five minutes, and to about 170° F in ten minutes (this was estimated by a blank run using a block containing a copper-constantan thermocouple in place of a cord). After flexing for a predetermined time, the blocks were allowed to stand for at least 24 hours and then tested for adhesion.

VISCOSITY

Ostwald's method was used, the reference liquid being distilled water; measurements were carried out at 20° C.

SURFACE TENSION

Jaeger's method was used, the reference material again being water; determinations were made at 20° C.

SEDIMENTATION

The rate of settling of some of the solutions was estimated by allowing an 8-inch column of solution to stand undisturbed at room temperature in a stoppered cylinder. At the outset, and after a period of seven days, a sample of solution was pipetted out from a point about 1 inch below the surface of the liquid, and its solids content was determined by evaporation. Duplicate measurements were made and the average taken. The drop in percentage solids content in this part of the column was taken as indicating the rate of sedimentation.

STIFFNESS OF CORD

This property was determined by an empirical test, in which a piece of cord was used for damping the swing of a compound pendulum. A length of cord

was fixed in a grip with 0.5 inch projecting vertically. The pendulum was made to strike the cord at the lowest point of its swing, and at this point the interference between the cord and the pendulum was 0.1 inch. The number of oscillations noted while the angle of swing was damped from 20° to 10° was taken as an indication of the stiffness.

RESULTS

EFFECT OF VARIATION IN CASEIN CONTENT

Seven solutions, in which the concentrations of casein and borax varied progressively, were tested and used for treating lengths of cord taken from the same sample. The compositions of the solutions, their properties, and results of tests of cord stiffness and adhesion before and after flexing are given in Table I. The flexing time was 10 minutes.

Solution A contained a small but unknown quantity of casein by virtue of its addition during the manufacture of the dispersed reclaim. The surface tension was unaffected by the change in casein content and, therefore, there was no appreciable variation in the ease of wetting of the cord. The viscosity, on the other hand, increased substantially as the casein content was increased.

TABLE I

	A g.	B g.	C g.	D g.	E g.	F g.	G g.
Casein	0	10	20	30	40	50	60
Borax	0	2	4	6	8	10	12
40% *Hevea* latex	120	120	120	120	120	120	120
Dispersed reclaim	180	180	180	180	180	180	180
Water	720	720	720	720	720	720	720
Surface tension (dynes per cm.)	50	51	50	50	51	48	50
Viscosity (millipoises)	13.5	15.9	21.7	26.7	32.0	44.9	61.4
Sedimentation (decrease in percentage concentration after 7 days)	4.6	3.1	3.1	3.1	3.3	2.7	2.1
Stiffness of cord (number of oscillations of pendulum)	31	25	23	20	19	17	16
Adhesion (lbs.)	8.4	10.0	10.1	11.0	10.5	9.0	8.4
Adhesion after flexing (lbs.)	5.9	9.1	8.5	11.1	11.0	9.3	9.0

As would be expected, it was found by microscopical examination of the cross-section of the treated cords that impregnation into the body of the cord decreased fairly regularly throughout the series from A to G. The first addition of casein produced a marked drop in sedimentation rate, but thereafter little change took place till the higher additions of casein resulted in considerable increase in viscosity. For convenience in handling this type of solution under factory conditions, it would appear desirable to use at least as much casein as represented by solution B. An undesirable feature of the high casein solutions is the stiffening of the cord which results from their use. This makes the calendering and tire building processes more difficult, and may also give rise to structural failure of the tire during service, owing to reduction in fatigue life.

The adhesion results showed that there is an optimum quantity of casein for maximum adhesion strength. After flexing the figures still show a maximum, but the effect of casein in increasing the resistance to fatigue is well illustrated. The adhesion for cord A dropped by about 30 per cent as a result of flexing, but in the case of G, which gave an unflexed value equal to A, there was no drop (the apparent improvement in adhesion on flexing cords D, E, F, and G is within the limits of experimental error). The efficacy of solutions B to G may,

however, be judged by the fact that in a similar test on untreated rayon the average adhesion value dropped from 5.2 to 1.9 lbs. under the relatively less severe flexing conditions of 15 minutes at 135 lbs. per sq. in.

EFFECT OF VARIATION OF LATEX AND DISPERSED RECLAIM CONTENT

The next series of dip solutions contained a fixed amount of casein, but the relative amounts of latex and dispersed reclaim were varied. The proportion of rubber hydrocarbon in the solution was kept approximately constant throughout the series. The solutions and treated cords were subjected to the same tests as before; the results are contained in Table II. The flexing time was again 10 minutes.

TABLE II

	H	J	K	L	M
	g.	g.	g.	g.	g.
Casein	30	30	30	30	30
Borax	6	6	6	6	6
40% *Hevea* latex	240	180	120	60	0
Dispersed reclaim	0	90	180	270	360
Water	780	750	720	690	660
Surface tension (dynes per cm.)	50	50	50	51	52
Viscosity (millipoises)	14.8	17.8	—	19.1	23.0
Sedimentation	0	2.0	3.5	4.6	6.0
Stiffness of cord	21	19	20	23	21
Adhesion (lbs.)	10.5	12.2	12.4	13.6	12.7
Adhesion after flexing (lbs.)	9.4	11.6	12.7	12.2	14.0

The surface tension was unaffected by replacement of 40 per cent latex by dispersed reclaim, but the viscosity increased. The tendency for settling out increased markedly as the reclaim content was raised. The change from latex to reclaim had no effect on the flexibility of the cord.

The adhesion given by all the solutions was good, but substitution of latex by reclaim gave a small definite improvement. The resistance to flexing was very good in each case.

EFFECT OF VARIATION OF LATEX AND CASEIN

In the previous two sections the solutions were rich in rubber, and contained relatively small proportions of casein. Four solutions were now made up in which the ratio of rubber to casein was varied through a wide range; the rubber was in the form of latex only, and no reclaim was employed. In this series, adhesion tests only were carried out, and the flexing time was again 10 minutes. The results are given in Table III.

The total solids content of each of the four solutions was 15 per cent. Dips N and R, containing only casein and rubber, respectively, gave low adhesion values, especially after flexing. All cords in this experiment suffered considerable reduction in adhesion, but P and Q were definitely superior to N and R in

TABLE III

	N	P	Q	R
	g.	g.	g.	g.
Casein	150	100	50	—
Borax	30	20	10	—
60% *Hevea* latex	—	100	200	300
Water	1,020	980	940	900
Adhesion (lbs.)	6.4	7.9	9.8	7.5
Adhesion after flexing (lbs.)	2.9	5.0	5.3	3.3

this respect. The best dip was Q, which was of fairly conventional composition except for the replacement of reclaim by latex.

EFFECT OF ADDITION OF WETTING AGENTS

Wetting agents added to the dip solution lower the surface tension and thereby assist in the uniform application of the adhesive. Various wetting agents were added to the solution C, and the resulting solutions were used for treating rayon cord. Each wetting agent was added in the proportion of 1 part by weight to 100 parts of solution. Greater amounts of sulfonated laurol were also employed. The results of measurements of surface tension and adhesion are given in Table IV; 8 minutes flexing time was used for this series.

TABLE IV

	C	S	T	U	V	W	X	Y	Z
Surface tension (dynes per cm.)	50	37	41	39	39	47	39	34	32
Adhesion (lbs.)	13.2	10.2	7.3	8.9	9.0	9.0	9.3	6.5	5.0
Adhesion after flexing (lbs.)	8.0	6.5	2.4	4.1	4.8	4.9	2.6	1.9	1.2

The materials added are shown below:

Solution C No wetting agent added
Solution S Vulcastab-OT
Solution T Petromor Pale A
Solution U Petrosol Powder
Solution V Faceamol
Solution W Triethanolamine
Solution X Sulfonated Laurol
Solution Y Sulfonated Laurol (2 parts/100 of solution)
Solution Z Sulfonated Laurol (5 parts/100 of solution)

The materials added varied in their effect on the surface tension. They all had an adverse effect on the adhesion of the cord to rubber; the drop in adhesion was least with Vulcastab-OT. In each case flexing caused a considerable drop in adhesion, very poor adhesions after flexing being given by some of the cords treated with solutions containing a wetting agent. Solutions Y and Z gave the worst adhesion results of the series, but contained quantities of sulfonated laurol in excess of that normally employed. The results with these two solutions, however, serve to emphasize that caution is necessary when adding a wetting agent to this type of dip.

VARIATION IN METHOD OF APPLICATION OF ADHESIVE

The results in Tables I and III show that there is an optimum proportion of casein to rubber in the solution for maximum adhesion to be obtained. This could be explained on the supposition that casein acts as a specific adhesive for rayon, while the rubber component gives the necessary affinity for the surrounding rubber. At high casein concentrations the affinity of rubber for the adhesive film would then be expected to fall off, while at high rubber concentrations the adhesion between rayon and adhesive film would be small. With these considerations in mind, an experiment was designed for two solutions of the compositions given in Table V, containing, respectively, major proportions of casein and of latex.

TABLE V

	A_1 g.	B_1 g.
Casein	100	25
Borax	20	5
60% *Hevea* latex	50	200
Water	830	770

Cords were dipped in each of these two solutions in the usual manner. A portion of the cord dipped in A_1 was then dipped in B_1, and similarly a portion of that dipped in B_1 was treated with A_1. If the above suggestion is correct, the cord sample dipped successively in A_1 and B_1 would be expected to give the best adhesion of the four, since the adhesive surface in contact with rayon would be rich in casein and that in contact with rubber would itself contain a large proportion of rubber. The adhesions were tested in the ordinary way, a flexing time of four minutes being employed. The results are given in Table VI.

TABLE VI

Cord treatment	A_1	B_1	A_1 followed by B_1	B_1 followed by A_1
Adhesion	6.0	8.9	9.7	7.9
Adhesion after flexing (lbs.)	4.0	7.2	9.3	4.5

It is seen that the best adhesion, and also the best resistance to flexing, was, in fact, given by the cord treated with A_1 followed by B_1. A further experiment was now carried out with solutions containing only casein and latex, respectively, as in Table VII.

TABLE VII

	C_1 g.	D_1 g.
Casein	100	—
Borax	20	—
60% *Hevea* latex	—	400
Water	1080	500

The plan of the experiment was exactly like the previous one, except that a fifth cord which had been dipped in a mixture of equal volumes of C_1 and D_1 was included; such a mixture is analogous to a conventional type of latex-reclaim-casein solution. The adhesion results are shown in Table VIII. The

TABLE VIII

Cord treatment	C_1	D_1	C_1 followed by D_1	D_1 followed by C_1	C_1 and D_1 mixed
Adhesion (lbs.)	6.0	6.1	6.3	6.2	8.2
Adhesion after flexing (lbs.)	1.7	3.1	6.5	3.2	7.8

flexing time was 8 minutes under a load of 135 lbs. per sq. in.; the reason for using this less severe load was the poor resistance to flexing of some of the bonds, especially that given by the cord dipped in C_1 alone.

In this case the first four cords showed almost the same adhesion before flexing. The markedly superior resistance to flexing given by the cord dipped in C_1 followed by D_1 suggests, however, that this type of treatment was the

best of the four. Dipping in the mixed solution gave definitely better adhesion than dipping in the two components successively. This was undoubtedly due to lack of adhesion between the two adhesive layers in the two-stage process; examination of the cord after pulling out suggested that the breakdown of the bond was at this point. With solutions A_1 and B_1, on the other hand, the difference in composition was far less marked and good adhesion between the adhesive layers was to be expected.

APPLICATION OF CEMENT COATING TO CORD TREATED WITH ADHESIVE

With cords dipped in an ordinary type of latex-reclaim-casein solution it was noticed that bond failure took place between the adhesive layer and the surrounding rubber, the cord after pulling out having very much the same appearance as before introduction into the rubber. Application of a solution of a vulcanizable rubber in solvent to a cord after dipping and drying has been found to improve the adhesion between rubber and adhesive layer. This is illustrated in the following experiment.

A 20 per cent cement was prepared by dissolving in benzene an unvulcanized sample of a casing rubber almost identical with that used in building up adhesion bars. A sample of cord was dipped in the solution C; part of this sample was then treated with the cement in the same apparatus as used for the first dipping. The adhesions of the two cords to rubber are given in Table IX. Flexing was for 4 minutes.

TABLE IX

Cord treatment	Solution C	Solution C and cement
Adhesion (lbs.)	10.7	13.3
Adhesion after flexing (lbs.)	10.7	12.4

The adhesion afforded by the cement-treated cord was definitely higher than that given by the cord dipped in latex-reclaim-casein alone; this is probably due to intimate mixing of the adhesive with the rubber deposited from the cement, assisted by swelling or partial solution in the hydrocarbon solvent of the rubber in the adhesive layer. Failure of the bond still took place preferentially between adhesive and rubber, however, showing that this part of the bond, though improved, was still the weakest link.

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SUMMARY

A good bond, resistant to flexing, is afforded between rubber and rayon cord by the interposition of a mixed casein-rubber film. In a series of solutions in which the proportion of rubber solids was kept constant and the quantity of casein varied progressively, it was found that there was an optimum amount of casein for maximum adhesion. Taking into consideration also the handling of the solution and the stiffening of the cord, it would appear that for an adhesive with the usual total solids content of 15 to 20 per cent, the ratio of casein to rubber hydrocarbon should be approximately 1:6.

When the rubber hydrocarbon is supplied by dispersed reclaim, the adhesion is a little higher than when latex is used. The most satisfactory solution from all points of view, however, contains approximately equal quantities of rubber hydrocarbon derived from the two sources.

Wetting agents may be employed to improve the uniformity of application of the adhesive. The amount used must be very small, otherwise the adhesion is impaired.

By dipping cord successively in casein and latex solutions and vice versa in the adhesive film, casein acts as a specific adhesive for rayon, whereas the rubber in the film gives the necessary affinity for the casing rubber which surrounds it. Treating a cord successively in a casein-rich mixture and then in a rubber-rich mixture appears to give a slightly better bond than the conventional treatment.

The subsequent application of a rubber cement to a cord dipped in latex-reclaim-casein solution results in an improvement in the bond.

A COMBUSTION METHOD FOR THE ESTIMATION OF CARBON BLACK IN COMPOUNDED RUBBER *

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INTRODUCTION

Methods in general use for the estimation of cabon black in compounded rubber fall into three groups:

(1) Those in which the rubber matrix, together with most of the compounding ingredients, are degraded or dissolved by hot nitric acid.
(2) Those that involve removal of the rubber and some compounding ingredients by means of an inert solvent, usually at an elevated temperature.
(3) Combustion methods in which the organic ingredients of the mixing and the rubber itself are destroyed by dry distillation in an inert atmosphere.

In all three procedures the carbon black is left in association with some mineral matter, and its final assay is carried out either by collecting the black and other unattacked residue in a filter crucible and weighing before and after combustion in an oxidizing atmosphere or by combusting the carbon black to carbon dioxide, which is collected and weighed in an absorption train of orthodox type.

Methods of the first group are very old established ones in rubber analysis, some of the earliest work having been carried out prior to 1914 by Jones[1]. The difficulty of retaining finely dispersed black on the filter pad has always been a troublesome feature, however, and as an improvement in this respect, Hammond[2] proposed the use of a filter pad of ignited kieselguhr supported on a layer of asbestos. This modification appears successful in a limited number of cases, but it is debatable whether the use of kieselguhr as a filtering medium provides any benefit over a properly compacted asbestos pad.[3]

The strongly adsorptive nature of many grades of carbon black leads to retention of decomposition products of the rubber, which in turn gives rise to fictitiously high values for the final carbon black figure. The older method of dealing with this positive error was to employ a purely empirical factor of approximately 0.95, a correction which appears to be a mean value between those for the highly adsorptive channel blacks and the low volatile lamp blacks, these blacks being the only types then in common use.

Alternatively, it has been proposed to remove such adsorbed substances by washing the separated carbon black with powerful solvents, such as hot acetone or chloroform[4]. The experience of this and other laboratories, however, is that the addition of such washing agents brings about immediate dispersion of the carbon black into the filtrate, necessitating troublesome refiltration with attendant inaccuracies. Even this modification, however, does not always solve

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the problem of adsorbed substances, for Oldham and Harrison[5] advocate the use of a correction factor of 0.95 in addition to washing the carbon black with acetone and chloroform.

In the present British Standards Institution method[6], interference from compounding ingredients that undergo a change in weight on heating, *e.g.*, china clay, is eliminated by oxidizing the separated carbon black in a combustion tube to carbon dioxide, which is collected and weighed in a soda-lime tube. Since the method estimates only "free" carbon, however, and in no way indicates the type of carbon black, the final adjustment of this figure to that for the carbon black originally present is entirely speculative.

The filtration difficulties encountered in nitric acid decomposition methods have led to proposals to use an inert solvent of high boiling-point for removal of the rubber matrix[7], some improvement is gained thereby, but organic matter is almost always entrained by the insoluble residue, and leads to high and variable results. A further disadvantage is that mineral ingredients of the mixing appear substantially in their original state, and their behavior in subsequent steps of the assay is to a large extent unpredictable. Solvent methods, therefore, on the whole have not received general support.

Combustion methods, compared with the other types mentioned, have the merit of speed, and mainly for this reason have attracted the attention of analysts, particularly for control testing. Namita[8] recommends a simple procedure of heating the compounded rubber for a specified time in a Rose crucible, into which a stream of nitrogen is fed. The loss in weight after reheating in an oxidizing atmosphere, after suitable correction, is assumed to represent carbon black.

The work of Marty[9] gives the first published information on modifications to the above simple technique. He worked with a closed tube in which the sample was contained in a boat, and a current of nitrogen was passed through the tube. The weight of carbon was finally determined by the difference method.

The investigations reported here were carried out with the object of improving still further the basic process proposed by Marty, while retaining as far as possible the advantages of speed, and the use of a small sample. The increasing adoption of rubberlike synthetic materials on the one hand, and the variety of grades of carbon black now available to manufacturers on the other, have sensibly increased the task of the analyst, and have revealed some of the shortcomings of the older methods. It is hoped that this paper will provide a useful line of attack on a problem of rapidly increasing importance and complexity.

EXPERIMENTAL

OUTLINE OF METHOD

A stream of nitrogen from a cylinder is fed through a purifying train into the first combustion tube, where pyrolysis of the volatile organic components of the rubber compound takes place. The residue in the combustion boat consists substantially of carbon black and mineral matter. After weighing, the boat is transferred to the second combustion tube, where oxidation to carbon dioxide takes place. The carbon dioxide is trapped in an absorption train of orthodox type and weighed. The boat is again weighed after the oxidation stage and the carbon content obtained by difference. It will be shown later how a consideration of these two values for the "carbon" leads to (1) a figure

for the total carbon black content of the compounds, (2) an indication of the type of carbon black used and (3) in favorable instances, an estimate of the ratio of blacks in a mixture of two types.

A detailed account of the apparatus and procedure, together with a representation of the assembly is given in the accompanying diagram.

INERT ATMOSPHERES AND GAS PURIFICATION

The first requirement of the gas that provides the inert atmosphere in the pyrolysis train is complete freedom from oxygen, since preliminary investigation showed the extreme susceptibility of the carbon to oxidation at the temperature employed. Coal gas and hydrogen, although otherwise suitable, were not considered on account of the serious fire risk.

Carbon dioxide meets the requirements of inertness and noninflammability, but there is no clear evidence that the reaction $CO_2 + C \rightarrow 2CO$, which takes place readily at 900° C, does not also proceed to some extent at the temperature of the initial pyrolysis (600° C). Also there is the possibility that the carbon dioxide might combine with certain metal oxides normally used in rubber compounding and seriously affect the weighings.

Compressed nitrogen from a cylinder, after further purification was found satisfactory. Although the "pure" material was used, preliminary experiments with carbon black alone indicated considerable continuous losses, due to traces of oxygen in the gas. Further purification was carried out by a two-stage process comprising (1) a pair of Drechsel washing bottles containing alkaline pyrogallol, and (2) a 30-cm. column of reduced copper turnings maintained at approximately 500° C. A small wash-bottle containing concentrated sulfuric acid was interposed between the pyrogallol and the copper.

Some purification of the oxygen used in the second stage is also necessary; this was accomplished by a pair of U-tubes containing soda-asbestos and Anhydrone.

COMBUSTION TEMPERATURES

For the initial dry distillation stage, a temperature must be chosen that will ensure the removal of the organic components of the compound without bringing about their breakdown into carbon, which would, of course, produce high values for the "carbon" content of the rubber compound. Too low a temperature entails an unduly long distillation time, and analytical errors may result from the failure to remove certain acid-forming substances such as sulfur. Nitrogen-containing compounds, such as acrylonitrile polymers, may give rise to oxides of nitrogen during the next (oxidation) stage, if not first removed by distillation; this also would lead to high results for the carbon content, unless the oxides of nitrogen are removed by a suitable reagent.

A temperature of 600° C was found most suitable, and it was concluded after investigation that a variation up to +30° was permissible. A total heating time of 10 minutes was found adequate to remove volatile substances at this temperature.

In the oxidation tube a temperature of 900° C for 15 minutes was found suitable. Below 900° C, complete oxidation of the carbon becomes uncertain under the experimental conditions employed; higher temperatures tend to cause rapid deterioration of the furnace windings and to give rise to difficulties with fusion of the copper oxide tube filling.

The amount of inherent volatile matter of the carbon black that is evolved

over the range 600° to 900° C is used to indicate the identity of the type of carbon black used in the compound, and from this and the fixed carbon content as determined from the weight of carbon dioxide absorbed, the proportion of carbon black originally present in the compound may be calculated (see later).

ABSORPTION SYSTEMS

(1) *Nitrogen tube.*—The purpose of the absorption train at the exit here is merely to prevent the escape of unpleasant decomposition vapors from the rubber and compounding ingredients into the atmosphere of the laboratory. For this purpose Marty has suggested xylene as absorbent[10]; it was found necessary, however, with the high gas flow rates used, to draw off escaping vapors not trapped by the xylene by means of a filter pump.

(2) *Oxygen tube.*—The main purpose of this absorption train is, of course, to absorb quantitatively the carbon dioxide formed by the combustion of the carbon black. Soda-asbestos (Carbosorb brand) was the absorbing agent used, contained in a stoppered U-tube. To prevent interference from oxides of nitrogen, the U-tube is preceded by a small Arnold bubbler containing potassium permanganate solution and sulfuric acid, with an intermediate U-tube containing magnesium perchlorate for drying purposes. The absorption train is concluded by another Arnold bubbler containing concentrated sulfuric acid.

CALCULATION OF RESULTS

(1) *Carbon residues from rubber and organic compounding ingredients.*—For quantitative results to be obtained by the method outlined, it is of obvious importance that organic components of the compound should leave either no residue at all apart from mineral matter after heating in nitrogen at 600° C, or should leave a constant proportion of carbonaceous residue whose influence on the final carbon figure can be calculated.

From none of the rubbers and rubberlike materials investigated were the nonmineral components completely volatilized. A list of the polymers tested, and the proportion of residual carbon formed, is given in Table I.

TABLE I

Type of polymer	C (%)*	
Natural rubber, plantation crepe	0.27	0.27
Natural rubber, smoked sheet	0.24	0.22
Butadiene—styrene copolymer (GR-S)	0.23	0.22
Isobutene—isoprene copolymer (GR-I)	0.10	0.10
Butadiene—acrylonitrile copolymer (Standard Perbunan)	1.5	1.5
Butadiene—acrylonitrile copolymer (Perbunan 35)	1.9	1.9
Butadiene—acrylonitrile copolymer (Hycar O.R.15)	3.6	3.7
Thioplast (Thiokol FA)	2.6	3.1
Polyvinyl acetate	2.7	2.6
Polyvinyl chloride	5.7	6.1
Chlorobutadiene (Neoprene)	15.4	12.3

* This represents the proportion of residual carbon after heating the polymer in nitrogen at 600° C for 10 minutes.

For most of the materials the amount of residual carbon produced is small and reasonably constant in amount, and for natural rubber, GR-S, and GR-I, little error would be introduced by omitting this correction from the subsequent calculation.

The butadiene-acrylonitrile series show distinctly higher values and also some variation between different grades. It becomes imperative, therefore, when determining carbon black in compounds based on these materials, to make a correction for the amount and type of rubber present. Experience with these compounds has shown that for this reason it is unwise to ascribe a higher degree of accuracy than ±2 per cent of the carbon black content; with low loadings, for example about 5 per cent of black, the experimental error may be even higher.

As would be expected, the chlorine-containing polymers offer considerable resistance to dry distillation, and with them the residual carbon is undesirably high and inconsistent in amount. It would seem, therefore, that the method is inapplicable to these polymers, and further investigations with them were not pursued.

Most compounding ingredients of an organic nature are extractable with acetone or chloroform, and hence by determining the carbon black content on the extracted material, interference from these sources may be avoided. Factice (sulfur-vulcanized oil), however, resists extraction with these solvents, but dry distillation of this material has shown it to be almost completely volatile, the residual carbon after combustion in nitrogen being constant at about 0.5 per cent. As factice is used in rubber compounding to only a minor extent, interference from this source is usually negligible.

(2) *Influence of inorganic fillers.*—The majority of inorganic compounding ingredients likely to be encountered in rubber compounded with carbon black do not change in weight between 600° and 900° C. Thus, magnesium carbonate readily loses carbon dioxide below 600° C, and its presence therefore does not influence subsequent weighings.

China clay loses 10 per cent of its weight at 600° C, and a further 2 per cent at 900° C. In the method described, the loss in weight on heating in oxygen, therefore, will be increased by an amount corresponding to 2 per cent of the clay present, and in making the final computation of the original carbon black content, a correction must be applied, based on the china clay content of the compound.

Calcium carbonate is not appreciably decomposed below 600° C, but loses all its combined carbon dioxide between 600° and 900° C. The carbon dioxide thus liberated is absorbed in the soda-asbestos tube and must be corrected for in the final result by computing its value from the amount of calcium carbonate present.

(3) *Volatile matter in carbon black.*—After making due allowance for the foregoing considerations, it might be expected that the weight of carbon dioxide absorbed by the soda-asbestos would bear a strict stoichiometric relationship to the weight of carbon black after the initial heating in nitrogen, and be proportional to the loss in weight during the oxidation stage. It might, therefore, appear unnecessary to utilize both the loss of weight in the oxidation stage and the weight of carbon dioxide absorbed to arrive at a figure for the carbon black content. The influence of the volatile matter in the carbon black on the relationship between these values is, however, a significant one, and must be considered in some detail.

Volatile matter, in this connection, is the term given to the gases adsorbed at the surface of the carbon particles, which can be successively removed at rising temperature levels. These gases range from oxides of carbon that begin to come off at about 500° C to the hydrocarbons and hydrogen, for the elimination of which temperatures up to 1400° C are considered necessary by some

workers. With channel blacks the proportion of such adsorbed gases may be considerable, frequently exceeding 6 per cent of the total weight, but lamp blacks, acetylene black, and most blacks produced by the furnace process have a low volatile content. The amount of volatile matter attached to any particular type of black is one of its most characteristic features, and it provides a ready means of differentiation between (for example) channel blacks and furnace blacks.

The evolution of volatile matter for the purpose of the present investigation has been studied at 600° and 900° C. Volatile matter evolved below 600° C is lost to the atmosphere (together with decomposition products of the organic materials in the rubber compound), but must be allowed for when computing the weight of carbon black originally present. Since, however, the extent of this volatile fraction is not actually determined, it plays no direct part in identifying the black used. Of the volatile matter evolved over the temperature range 600° to 900° C, which forms the larger proportion of the total volatile matter, some is oxidized to carbon dioxide and is weighed in the soda-asbestos tube, whereas the remainder is nonoxidizable, and is represented by the discrepancy between the carbon as determined by the difference in weight before and after oxidation, and the carbon as determined from the carbon dioxide formed. This nonoxidizable fraction, although only a part of the total volatile matter, is accurately determinable, is characteristic of the type of black, and forms the basis used in this investigation for the differentiation between types. Its amount is calculated as follows.

If the total weight of dry carbon black originally present in a rubber compound is W, and a, b, c, d and e have the following meanings:

a = weight of volatile matter evolved below 600° C
b = weight of volatile matter evolved over the temperature interval 600° to 900° C, and not oxidizable to carbon dioxide
c = weight of volatile matter evolved over the temperature interval 600° to 900° C, and oxidizable to carbon dioxide
d = weight of nonvolatile carbon
e = weight of carbon dioxide produced

then $$W = a + b + c + d$$

and $$0.2729 \times e = c + d;$$

hence $$W - a = b + 0.2729\, e$$

or $$b = (W - a) - 0.2729\, e$$

Since the term $(W - a)$ represents the difference in weight before and after oxidation, the value of b can be readily calculated.

Many of the commoner carbon blacks used in the industry have been examined in this way, and the data are presented in Table II.

It will be seen that the values of $100\, b/(W - a)$ in column (1) fall into two clearly defined groups, the high-volatile channel blacks, ranging from about 5 to 8 per cent, and the low-volatile furnace and lamp blacks, with figures usually below 3 per cent.

When the type of carbon black used has been determined by reference to Table II, it is a simple matter to make a correction for the total volatile matter. Column (2) of Table II shows the ratio of oxidizable carbon (*i.e.*, that which is weighed as carbon dioxide) to original carbon black for the same series of stand-

TABLE II

Column (1) shows values for nonoxidizable volatile matter evolved over the temperature range 600° to 900° C, calculated as a percentage of the carbon black after heating in nitrogen at 600° C.

Column (2) shows the proportion (per cent) of true carbon in the original black, calculated from the yield of carbon dioxide.

Sample	Type	(1) $\frac{b}{W-a}100$	(2) $\frac{0.2729\,e}{W}100$
Micronex	Channel	6.0	91.6
Kosmobile H.M.	Channel	5.6	91.3
Spheron-4	Channel	5.3	93.8
Spheron-6	Channel	7.9	90.7
Spheron-9	Channel	5.7	91.7
Dixiedensed H.M.	Channel	6.7	90.8
Dixie R.1	Channel	5.2	91.5
Spheron-C	Channel	4.5	93.6
Magecol	Lamp	0.2	97.4
Champion	Lamp	0.8	98.1
Statex-93	Furance	0.0	99.3
Statex-K	Furnace	3.4	96.0
Furnex	Furnace	2.3	93.4
P.33	Thermal	0.7	96.5
Seval	Thermal	2.3	97.1
Shawinigan	Acetylene	0.0	99.8

ard grades, and allowance has been made for the volatile matter lost below 600° C. Again, it will be seen that a greater correction is necessary with channel blacks than with other types, although the values do not follow a strict reslationship with the figures in column (1).

With binary mixtures of carbon blacks, a useful estimate of the ratio of the two components can be obtained. It is, of course, necessary with mixtures to know the types of black present, and the confidence to be placed in the final result is dependent on the difference in the value of b for the two components. The value of b for the mixture determined experimentally lies between the values for the two blacks considered separately according to the relative proportions of the blacks present. This ratio may be found from the following expression:

$$A = \frac{V - V_B}{V_A - V_B} \cdot 100$$

in which

A = proportion of carbon black A calculated as a percentage of the total black present
V = value of b for the mixture of blacks in the rubber as determined experimentally
V_B = value of b for carbon black B
V_A = value of b for carbon black A
} as given in Table II, column (1)

RESULTS

In Tables III, IV, and V, results are given for a series of unvulcanized and vulcanized rubber compounds. The behavior of the main types of carbon black

in association with the more commonly used polymers has been studied, and mixings have been chosen to illustrate the influence of whiting and china clay. All samples of carbon black were dried at 120° C for 4 hours before mixing into rubber.

The results were calculated in the manner already outlined, but for the sake of further clarity, intermediate stages in the calculation have been included in colum nar form.

Although the black loadings are nominal, care was taken to reduce as far as possible the errors often associated with small-scale compounding.

With the unvulcanized compounds, somewhat greater variation than seemed desirable occurred in the pale crepe series. The carbon black content in these abnormal cases was checked by the nitric acid decomposition method and the results confirmed this variation, indicating that lack of uniformity in the com-

TABLE III

UNVULCANIZED CHANNEL BLACK COMPOUNDS

(Micronex; $\frac{0.2729\ e}{W}\ 100 = 91.6$)

Polymer	(a)	(b)	(c)	(d)	(e)
Pale crepe	30	0.1026	0.1050	0.0002	30.2
	30	0.1014	0.1035	0.0002	30.2
	15	0.1186	0.0607	0.0002	15.0
	15	0.1048	0.0532	0.0002	14.9
	7.5	0.1134	0.0278	0.0003	7.0
	7.5	0.1040	0.0254	0.0003	7.0
	3.75	0.1168	0.0148	0.0003	3.5
GR-S	15	0.1250	0.0640	0.0003	15.0
	15	0.1774	0.0907	0.0004	15.0
	7.5	0.1263	0.0326	0.0003	7.4
	7.5	0.1190	0.0309	0.0003	7.5
GR-I	15	0.1212	0.0615	0.0001	15.0
	15	0.1447	0.0734	0.0001	15.0
	7.5	0.1094	0.0279	0.0001	7.5
	7.5	0.1170	0.0297	0.0001	7.5
Perbunan	15	0.1121	0.0616	0.0014	15.0
	15	0.1008	0.0555	0.0013	15.0
	7.5	0.1303	0.0394	0.0018	7.5

pound was responsible. Thereafter, a stricter mixing technique was followed, and subsequent results showed a higher degree of precision.

The black loadings in the vulcanized compounds, nominally 15 per cent, were actually obtained by check-weighing, and the experimental results show a degree of accuracy, even in presence of china clay and calcium carbonate, that compares favorably with that given by the nitric acid decomposition method. Unfortunately the assessment of accuracy by direct comparison with laboratory mixed compounds is not valid beyond a certain point, owing to the difficulty of preparing compounded rubber whose actual composition is itself beyond all doubt.

With binary mixtures of carbon black, substitution of the appropriate values for V_A and V_B in the formula $A = 100\ (V - V_B)/(V_A - V_B)$ requires a knowledge of the type and brand of the two separate components, and since such data are unlikely to be available for compounded rubbers of unknown

TABLE IV

UNVULCANIZED LAMP BLACK COMPOUNDS

(Magecol; $\frac{0.2729\ c}{W}\ 100 = 97.4$)

Polymer	(a)	(b)	(c)	(d)	(e)
Pale crepe	30	0.1071	0.1140	0.0002	29.6
	30	0.1018	0.1086	0.0002	29.7
	15	0.0777	0.0417	0.0002	14.8
	15	0.0893	0.0478	0.0002	14.8
	7.5	0.0840	0.0231	0.0002	7.4
	7.5	0.0920	0.0249	0.0002	7.3
	3.75	0.0744	0.0107	0.0002	3.83
	3.75	0.0592	0.0085	0.0002	3.75
Smoked sheet	15	0.1258	0.0676	0.0002	14.9
	15	0.0954	0.0514	0.0002	15.0
	7.5	0.1260	0.0341	0.0003	7.4
	7.5	0.1321	0.0359	0.0003	7.4
GR-S	15	0.1136	0.0609	0.0002	14.8
	15	0.2038	0.1100	0.0004	14.9
	7.5	0.1042	0.0284	0.0002	7.4
	7.5	0.1026	0.0279	0.0002	7.4
GR-I	15	0.1326	0.0709	0.0001	14.9
	15	0.1269	0.0680	0.0001	14.9
	7.5	0.1130	0.0303	0.0001	7.4
	7.5	0.1200	0.0321	0.0001	7.4
Perbunan	15	0.1040	0.0603	0.0014	14.9
	15	0.1108	0.0643	0.0014	14.9
	7.5	0.1115	0.0354	0.0016	7.5
	7.5	0.1200	0.0381	0.0017	7.5

KEY TO TABLES III AND IV

Column (*a*) Nominal carbon black loading (per cent)
Column (*b*) Weight in grams of the sample taken for test
Column (*c*) Weight of CO_2 obtained
Column (*d*) Correction for carbonaceous residue from the polymer as determined by consulting Table I
Column (*e*) Carbon black found (per cent)

TABLE V

VULCANIZED COMPOUNDS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Smoked sheet	67.5	77.5	77.5	67.5	—	—	—
GR-S	—	—	—	—	77.5	—	—
Perbunan	—	—	—	—	—	74.0	74.0
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	1.0	1.0	1.0	1.0	1.0	2.0	2.0
Mercaptobenzothiazole	1.0	1.0	1.0	1.0	1.0	1.5	1.5
Zinc oxide	3.0	3.0	3.0	3.0	3.0	5.0	5.0
China clay	10.0	—	—	—	—	—	—
Calcium carbonate	—	—	—	10.0	—	—	—
Furnace black (Statex-93)	14.5	—	—	—	—	—	—
Lamp black (Champion)	—	—	15.2	—	—	—	—
Acetylene black	—	14.5	—	—	—	—	—
Channel black (Spheron-9)	—	—	—	15.8	—	—	—
Channel black (Kosmos H.M.)	—	—	—	—	15.8	—	—
Furnace black (Statex-K)	—	—	—	—	—	16.2	—
Channel black (Spheron-C)	—	—	—	—	—	—	16.5
Carbon black by experiment	14.3	14.0	15.3	15.5	16.0	16.6	16.9
Value of $\frac{b}{W-a} \cdot 100$	0	0	0.23	5.8	5.6	3.2	4.4

origin, the method of evaluating mixtures can usually be applied with confidence only to routine control analysis where the qualitative nature of the carbon black is not in doubt. The calculated values of A are very sensitive to the substituted values of V_A and V_B, and experience has shown that it is unwise to substitute even the mean values for each class of black, as values of A obtained in this way may vary up to about 20 per cent.

When the precise grades of carbon black are known, however, and the appropriate values of V_A and V_B can be substituted, a useful estimate of the ratio can be obtained. Thus, for a mixing containing Micronex ($V = 6.0$) and Magecol lamp black ($V = 0.2$), the value of V determined experimentally for the mixture was 3.7. Substituting these values in the formula, the value of A becomes 40 per cent, indicating a 40:60 lamp black-channel black mixture. Such good agreement, however, is regarded as fortuitous and a degree of accuracy within ± 5 per cent, even in favorable circumstances, is not claimed.

In a second example it was known that a mixture of Micronex and Statex-K furnace black had been incorporated in a rubber mixing; it was required to find the ratio of these components. The following values were substituted in the formula:

V_A	3.4
V_B	6.0
V	4.6 (determined experimentally)

The value of A is calculated as 46 per cent, which suggests a mixture of approximately equal parts of Micronex and Statex-K. For reasons stated previously, however, the limits of variability of the ratio might reasonably be expected to range from 40 to 50 per cent of Statex-K.

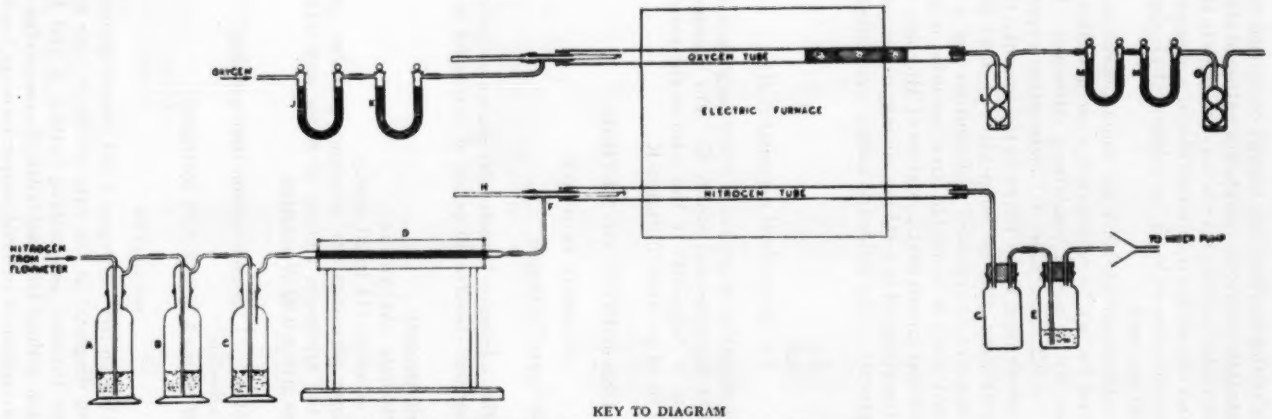
DESCRIPTION OF METHOD

REAGENTS REQUIRED

(1) "Oxygen-free" or "pure" nitrogen.
(2) Oxygen.
(3) Alkaline pyrogallol solution—Dissolve 50 grams of pelletized caustic potash in 100 cc. of water and dissolve 30 grams of pyrogallol in the solution.
(4) Xylene.
(5) Concentrated sulfuric acid.
(6) Magnesium perchlorate (Anhydrone).
(7) Soda-asbestos, Carbosorb (14 to 20 mesh).
(8) Acidified potassium permanganate solution—Dissolve potassium permanganate crystals in the minimum volume of water and dilute with concentrated sulfuric acid to give a 0.02 N solution.
(9) Cupric oxide
(10) Platinized asbestos } for combustion tube packing.
(11) Ignited Gooch asbestos
(12) Copper turnings reduced *in situ* with hydrogen.

APPARATUS

Nitrogen supply.—"Oxygen-free" nitrogen is fed from a cylinder, through a flowmeter (not shown on diagram) at the rate of 500 cc. per minute. It is passed then through two Drechsel gas-washing bottles, A and B, containing alkaline pyrogallol solution, a third Drechsel bottle, C, containing concentrated sulfuric acid and a 30-cm. column of reduced copper turnings heated by a small



KEY TO DIAGRAM

A, B	Alkaline pyrogallol wash-bottles	J	U-tube containing anhydrone
C	Concentrated sulphuric acid wash-bottle	K	U-tube containing soda asbestos
D	Heater for reduced copper column	L	Acidified permanganate wash-bottles
E	Absorption bottle containing xylene	M	U-tube containing anhydrone
F	T-piece entry tube	N	U-tube containing soda-asbestos
G	Bottle for trapping effluent gases	O	Sulphuric acid bubbler
H	Silica rod for manipulating boat		

furnace, D. The purified gas is admitted to the combustion tube via a T-piece, F, through which passes a silica rod, H, with a hooked end of nickel-chromium wire for manipulating the combustion boat. G is a trap for collecting condensible vapors formed during the pyrolysis, and E is the final absorption vessel containing xylene. Residual gases are drawn away through a small funnel attached to a filter pump.

For the oxidation train oxygen is taken from a cylinder and purified by passing through two U-tubes, J and K, containing Anhydrone and soda-asbestos, respectively. As in the first tube, the boat is manipulated by means of a silica rod sliding in a glass T-piece. The combustion tube is packed in the positions shown on the diagram with (*a*) platinized asbestos and (*b*) cupric oxide, with intermediate and supporting packings of Gooch asbestos.

L is an Arnold bubbler containing acidified potassium permanganate, and after passing through this and a U-tube, M, containing Anhydrone, the effluent gases are passed through a U-tube, N, containing soda-asbestos, in which the carbon dioxide is absorbed. The train is terminated by an Arnold bubbler, O, containing concentrated sulfuric acid, which serves to indicate the rate of oxygen flow.

PROCEDURE

Samples are given a prior extraction with acetone and, if mineral rubber is thought to be present, chloroform extraction is necessary also, these operations being carried out by standard methods[10].

Weigh accurately an amount of sample equivalent to approximately 0.1 gram of the original sample into a silica combustion boat (5 by 1 cm.) and place just inside the cool end of the nitrogen combustion tube, which is then closed with the entry fitting. Pass nitrogen into the train at the rate of 500 cc. per minute, switch on the preheater furnace, D, and the main electric furnace, and allow them to reach temperatures of 500° and 600° C, respectively. When these temperatures have been attained, push the combustion boat slowly forward by means of the silica rod, until in 5 minutes it reaches the hot zone of the furnace, where it is heated for a further 5 minutes. Then return the boat to its original position at the end of the tube, cool for 10 minutes with nitrogen still passing, and weigh if it is required to determine the type of black or the proportions of black present in a binary mixture.

Now transfer the boat and contents to the oxygen tube, to which oxygen is admitted at the rate of 25 cc. per minute, and when the temperature of the furnace has reached 900° C, push the boat into the hot zone for 15 minutes. Disconnect from the train the soda-asbestos absorption tube, which has previously been weighed, and reweigh, and calculate the corrected figure for carbon dioxide as already described under "Calculation of Results."

After the absorption tube has been disconnected remove the entry fitting, take out the boat, cool in a desiccator and weigh. The loss of weight of the boat and its contents on oxidation is equal to $(W - a)$ in the expression $0.2729x/(W - a)$.

SUMMARY

The method described in this paper is based on the removal of volatile organic ingredients of the compound by heating in a current of purified nitrogen and, on the subsequent combustion of the carbon black to carbon dioxide, which is collected and weighed. The effect of the adsorptive nature of the carbon

black has been studied, and the volatile components of many of the standard grades of carbon black used in the industry have been determined under the experimental conditions used.

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A TACKMETER FOR RUBBER TESTING *

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DISCUSSION

In the hand test for tackiness commonly used, two surfaces of the compound are pressed together for a short time and are then separated, the force required for separation giving a measure of the tackiness of the compound. The magnitude of the separating force depends largely on such factors as the load applied to the contacting surfaces, the duration of application of the load, and the surface area in contact, but none of these factors can be controlled within reasonable limits of reproducibility. Moreover, the results of this test can be recorded only in rather general terms such as "fair", "good", so recorded results may vary from one operator to another and they depend very largely on the experience of the individual operator. It thus becomes evident that in any investigation which calls for the evaluation of the tack properties of a fair number of different compounds, some method of test is required in which the personal element is entirely eliminated. In the course of an investigation into the tackiness of GR-S compounds, Busse, Lambert, and Verdery (*J. Applied Physics* **17**, 376 (1946)) designed an apparatus which enabled the measurement of tack values to be put on a quantitative basis, and the principles of the apparatus reported by them have been embodied in the tackmeter described below.

DESCRIPTION OF APPARATUS

In general it can be said that the apparatus is simply a motorized version of the original hand test. Means are provided for bringing the specimens into contact at a predetermined loading and for separating them, both the loading and the separating forces being recorded by scale pointers. The loading and separating cycle is completed in 2.4 seconds, but an automatic clutch mechanism which enables the specimens to be held in contact for any desired length of time is incorporated. The general arrangement of the instrument is shown in Figure 1 and the automatic clutch mechanism is shown diagrammatically in Figure 2. A fractional horse-power motor with a reduction gear-box is coupled to a driving shaft which carries a mild steel wheel with a knurled periphery. When the clutch is engaged, the drive is taken up by a large rubber-tired wheel which bears against the knurled driving wheel. The total gearing is such that this rubber-tired wheel rotates at 25 r.p.m. A single-web overhung crank is secured to the spindle of the final driven wheel, and this imparts a reciprocating motion to the two rods carrying the top specimen clamp through the medium of a slotted link. The lower specimen clamp is normally maintained in an arbitrary zero position by means of two pre-loaded extension springs, but it moves in a vertical plane under the action of the loading and separating forces

* Reprinted from the *Proceedings of the Second Rubber Technology Conference*, London, June 23–25, 1948, pages 224–232.

of the reciprocating top clamp. A nylon thread fastened to the lower clamp support rod drives a pointer on the front of the instrument, and this in turn drives two slave pointers which indicate the maximum values of the applied load and the separating force.

The diagram of the automatic clutch mechanism, Figure 2, shows the knurled driving wheel A, and the rubber-tired wheel B. The spindle C on

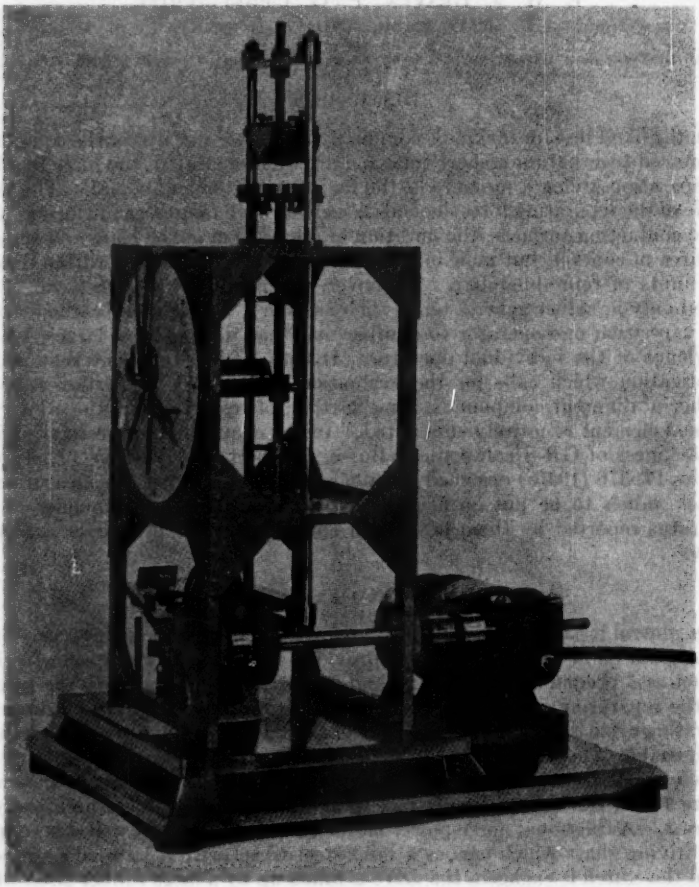

FIG. 1.—Tackmeter—three-quarter front view.

which B is mounted runs in bearings in the side plates D, and these side plates are pivoted on bolts E, which screw into a trunnion block F. The side plates D are connected by toggle links G to a control lever H, so that a pin-jointed link assembly is formed. If now the free end of the lever H is depressed the side plates D are rocked on their pivot bolts and the wheel B is carried over to bear against the driving wheel A. The downward travel of H is arranged so that

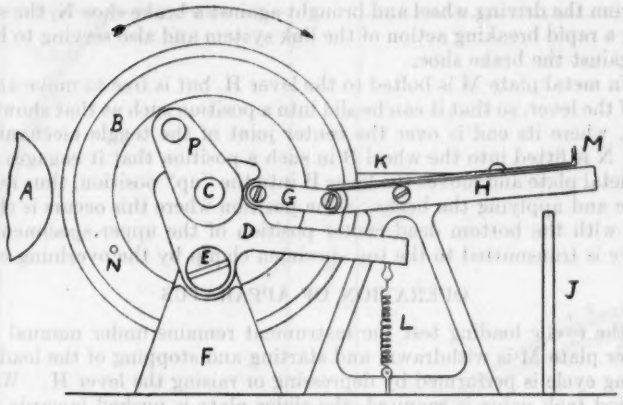

FIG. 2.—Diagram of automatic clutch mechanism.

the center pin of the link system lies above the centerline of the other two pins, thus making the toggle system self-locking in the driving position. A limit stop J is provided to prevent strain on the link system by excessive pressure on the lever H. On returning the lever H to the "up" position, the wheel B is with-

TABLE I

RECIPES USED IN TACK EVALUATIONS

GR-S tread	GR-S	100	parts by weight	
	Zinc oxide	3		
	Stearic acid	3		
	Spheron-9	50		
	Neozone-A	1		
	Captax	1		
	Dutrex-R	3.5		
	Sulfur	3		
GR-S premasticated 20 minutes in cold Banbury; composition reworked 20 minutes in cold Banbury				
Natural rubber tread	Smoked sheet	100		
	Zinc oxide	5		
	Stearic acid	1.5		
	Micronex	50		
	Neozone-A	1		
	Captax	1		
	Dutrex-R	3.5		
	Sulfur	3		
Smoked sheet premasticated 10 minutes on warm rolls; composition reworked 10 minutes on warm rolls				
Natural rubber extrusion compositions	Smoked sheet	100	100	100
	Zinc oxide	5	5	5
	Stearic acid	1	1	1
	Gastex	50	50	50
	Paraffin wax	0	5	10
	Altax	1.5	1.5	1.5
	Sulfur	2	2	2
Smoked sheet masticated 10 minutes on warm rolls; composition reworked 10 minutes on warm rolls				

drawn from the driving wheel and brought against a brake shoe K, the spring L ensuring a rapid breaking action of the link system and also serving to hold the wheel against the brake shoe.

A thin metal plate M is bolted to the lever H, but is free to move along the length of the lever, so that it can be slid into a position such as that shown in the diagram, where its end is over the center joint of the toggle mechanism. A steel pin N is fitted into the wheel B in such a position that it engages the end of this metal plate and moves the lever H into the "up" position, thus removing the drive and applying the brake. The position where this occurs is chosen to coincide with the bottom dead center position of the upper specimen clamp. The drive is transmitted to the top specimen clamp by the overhung crank P.

OPERATION OF APPARATUS

For the cyclic loading test the instrument remains under manual control. The slider plate M is withdrawn, and starting and stopping of the loading and separating cycle is performed by depressing or raising the lever H. When the long-period tack value is required, the slider plate is pushed inwards and the lever H is depressed. The apparatus thus runs until the specimens are in contact at the position of maximum loading, at which point the motor is automatically declutched. After the lapse of the desired period of time, the slider plate is withdrawn, and the control lever is depressed. The reciprocating cycle then continues from the point at which it was arrested.

CALIBRATION OF APPARATUS

The dial is calibrated from 0° to 180° on either side of the zero position, though this may well be altered to read grams directly. The magnitude of the

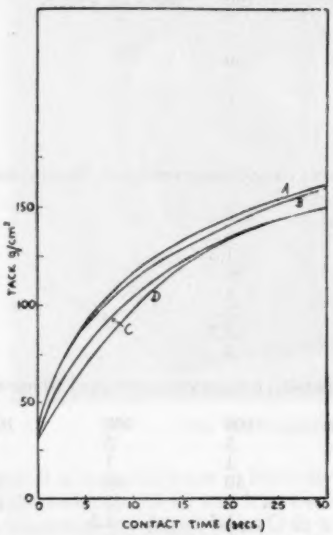

FIG. 3.—Natural rubber tire tread. No solvent. Curve A. Immediately after reworking. Curve B. 1 hour after reworking. Curve C. 24 hours after reworking. Curve D. 48 hours after reworking.

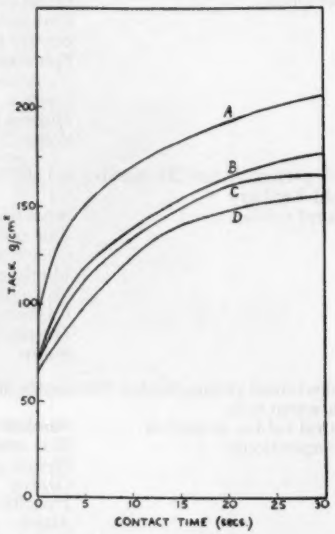

FIG. 4.—Natural-rubber tire tread. Solvent—Methylethyl ketone.

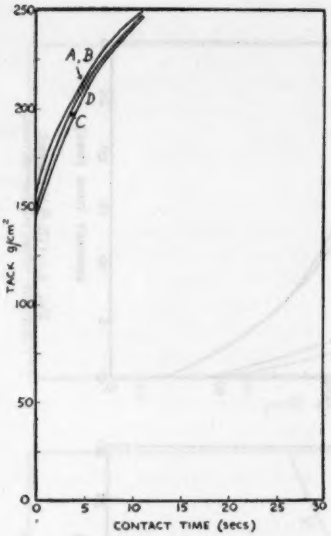

FIG. 5.—Natural-rubber tire tread. Solvent—Pool rubber solvent.

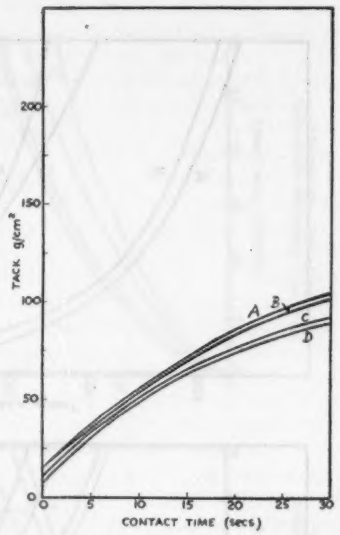

FIG. 6.—GR-S tire tread. No solvent.

loading force can be varied from 0 to 600 grams by adjustment of the screwed rod which carries the top specimen clamp. The linearity of the spring system was proved by applying dead weights to the lower specimen clamp and showing that the scale readings are strictly proportional to the load. The top specimen clamp is provided with a mask which ensures that the area of rubber in contact is limited to 0.8 sq. cm. It is therefore convenient to express tack values obtained from the apparatus in units of grams per sq. cm.

SOME APPLICATIONS OF THE TACKMETER

To demonstrate the use of this apparatus, some measurements were carried out on various compositions, which might be used in the manufacture of articles by lamination or by extrusion.

It is well known that an unvulcanized composition slowly loses its tackiness when left exposed to the atmosphere and (or) strong sunlight, and that this decrease of tack is still evident, though probably not very important, after the surfaces which are to be brought into contact have been moistened with a suitable liquid before building up a laminate. This effect is shown in natural rubber and GR-S tire tread compositions and natural rubber extrusion stocks containing various amounts of wax.

In the first group of figures, 3 to 5, for a natural rubber tire tread composition, it can be seen that methylethyl ketone is effective only if lamination is carried out immediately after milling, but even so it is far less effective than Pool rubber solvent, as might be expected. The curves in the latter case are very close together.

Figures 6 to 9 show similar experiments with a GR-S tire tread stock. Here, of course, the tack is considerably lower. Moistening with ethanol has a comparatively slight effect. Methylethyl ketone is rather more effective, while

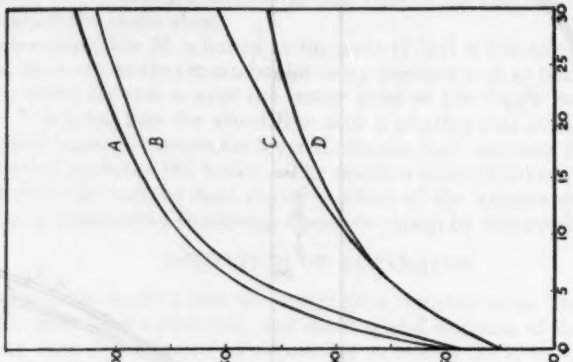

FIG. 9.—GR-S tire tread.
Solvent—Pool rubber solvent.

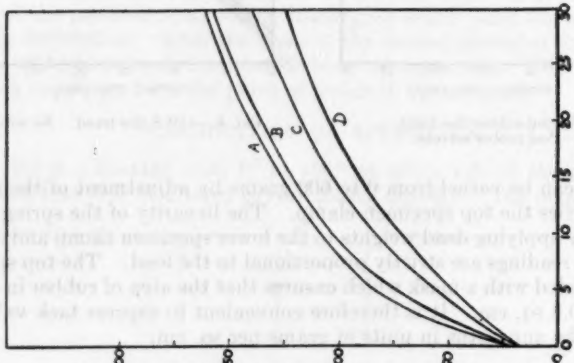

FIG. 8.—GR-S tire tread.
Solvent—methylethyl ketone.

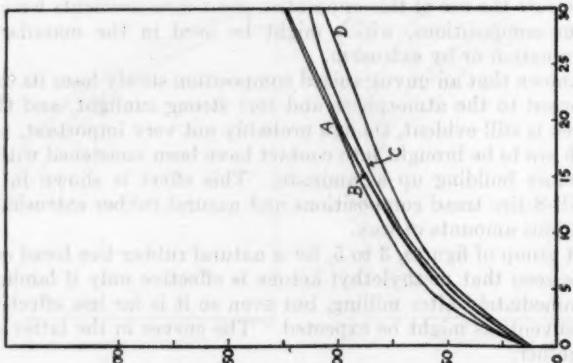

FIG. 7.—GR-S tire tread.
Solvent—ethanol.

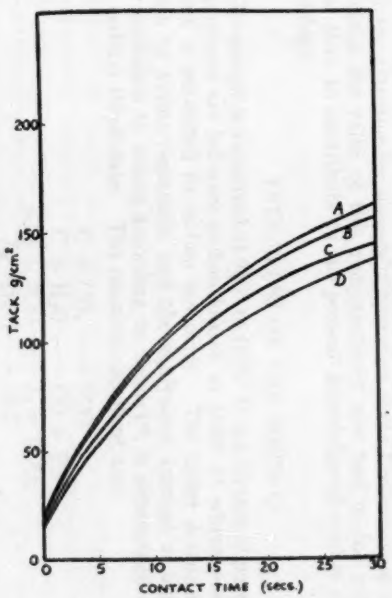

FIG. 10.—Extrusion compound. No solvent.

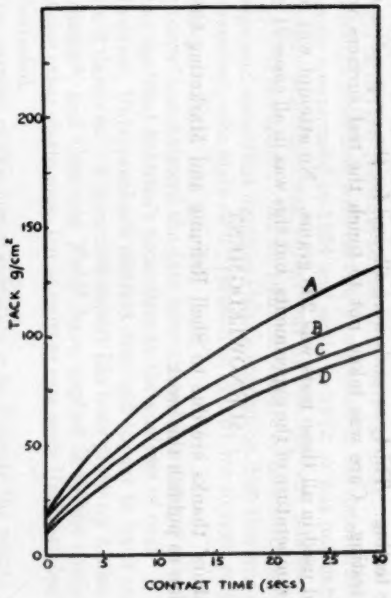

FIG. 11.—Extrusion compound. 5% wax. No solvent.

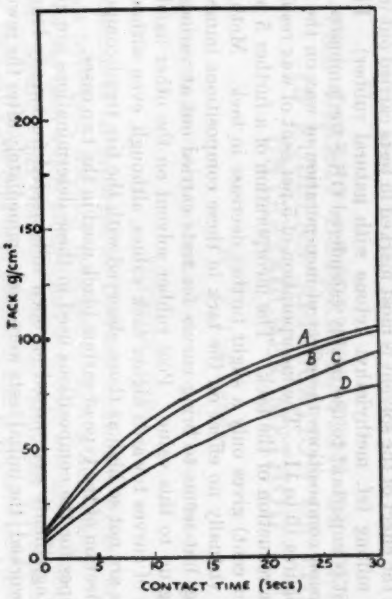

FIG. 12.—Extrusion compound. 10% wax. No solvent.

Pool rubber solvent is better still; in this case there is a wide spread among the curves, and the effect of the solvent is most marked in tests carried out immediately after milling (cf. methylethyl ketone with natural rubber). Figure 9 shows that it is important to use freshly calendered GR-S for laminates.

In extrusion compositions the effect of incorporation of wax on the tack is shown in Figures 10 to 11. The incorporation of 5 per cent of wax results in a considerable reduction of the tack. The incorporation of a further 5 per cent (total 10 per cent) gives only a slight further decrease in tack. Methylethyl ketone had virtually no effect on the tack in these compositions immediately after milling, but seems to bring curves for tests carried out at various times after milling up to this value. Pool rubber solvent on the other hand raises the families of curves towards higher tack values, although, even without wax, these values are not so high as those observed with the tire tread composition. This is a reflection of the type of carbon black used in the two cases.

The recipes for the compositions used in these determinations are given in Table 1. Ingredients were mixed on open rolls, rested for twenty-four hours and then reworked; the initial tests were made immediately after the reworking.

When liquids were used these were applied to the surfaces by means of a swab before testing. Thirty seconds were allowed for the evaporation of solvent before testing. Care was taken not to touch the test surfaces with the hand.

The load used in all these tests was 200 grams. No attempt was made to control the temperature of the experiments, but this was in all cases 21 $\pm$ 2° C.

ACKNOWLEDGMENT

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THE DIRECT DETERMINATION OF OXYGEN IN RUBBERS. APPLICATION OF THE UNTERZAUCHER METHOD *

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INTRODUCTION

Methods so far proposed for the determination of oxygen in organic compounds have been critically reviewed by Elving and Ligett[1]. Ter Meulen's method has been widely studied and developed and also applied to rubber by Cramer, Sjothun, and Oneacre[2], but only rarely has a precision or accuracy better than ±0.1 per cent been obtained, and it appears that hydrogenation is suited neither to the determination of traces of oxygen nor to the precise determination of oxygen contents of the order of 1 per cent.

Although reduction with carbon was applied to the determination of oxygen in organic compounds[3] in 1904 and again in 1912, it was not until 1939 that a satisfactory procedure was worked out by Schütze[4] and adapted to the microscale by Zimmermann[5]. An undesirable feature of Zimmermann's method was the large and somewhat empirical blank correction, but this was eliminated by Unterzaucher[6], who claimed a precision of ±0.01 for oxygen contents up to 1 per cent.

Spooner[7] has reviewed the data concerning the water gas reactions involved, and has modified Schütze's procedure to the analysis of coal.

However, Unterzaucher's method does not appear to have received the attention it deserves. A favorable report has been given by Aluise, Hall, Staats, and Becker[8], and Cole and Field[9] have applied it to the oxidation study of GR-S and other elastomers, but in neither case were Unterzaucher's claims fully substantiated.

The purpose of this communication is to indicate the points which require particular attention for successful operation of the Unterzaucher method and to emphasize the value of this comparatively new tool to the rubber chemist, rather than to contribute to the present knowledge of rubber chemistry and technology.

PRINCIPLES OF THE METHOD

The sample is vaporized at 950° to 1000° C in a stream of pure nitrogen and the products are led over carbon heated to 1100° C, whereby all the oxygen present is converted to carbon monoxide. The latter is oxidized to carbon dioxide by iodine pentoxide, and the equivalent amount of iodine liberated, after oxidation to iodate according to Leipert[10], is determined titrimetrically with sodium thisolufate. The reactions involved are:

$$C + CO_2 \longrightarrow 2CO$$
$$C + H_2O \longrightarrow CO + H_2$$
$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$
$$I_2 \rightarrow 2IO'_3 \longrightarrow 12\ I$$

* Reprinted from the *Proceedings of the Second Rubber Technology Conference*, London, June 23–25, 1948, pages 115–121.

Since one oxygen atom ultimately provides 2.4 iodine atoms for titration, we have 1 ml. 0.01 *N* thiosulfate = 0.0667 mg. oxygen, and the detection of 1 microgram of oxygen becomes possible.

The method is applicable to compounds containing nitrogen, sulfur, and halogens, interfering products of the two latter elements being removed by alkali before oxidation of the carbon monoxide.

APPARATUS AND PROCEDURE

The apparatus shown in Figure 1 differs from that described by Unterzaucher[11] in the arrangement for supplying and measuring the nitrogen stream and in the provision of a trap, whose use will be described later.

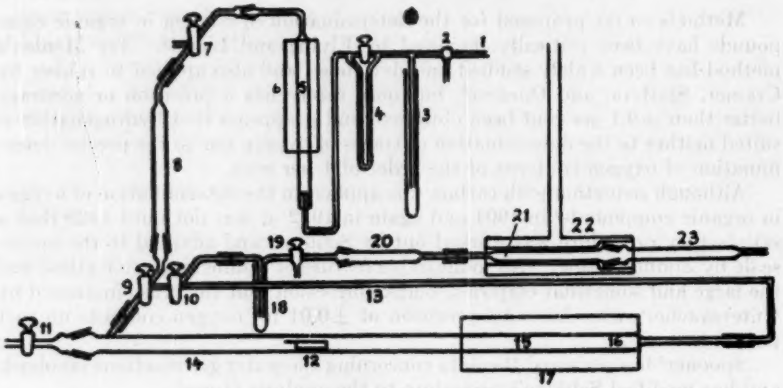

FIG. 1.—Diagram of apparatus.

1. Direct connection to reducing valve of cylinder containing commercial "oxygen-free" nitrogen (0.02 to 0.03% O).
3. Water-filled pressure regulator.
4. Friedrich pattern flowmeter.
5. Quartz preheater containing a 9 × 190 mm. section of wire form copper.
6. Sleeve heated electrically to 600° C.
2 and 7. Three-way taps for reduction of copper by hydrogen.
8. Scavenging tube, 11 mm. i.d. containing a 5-cm. section of 14–20 mesh indicating soda asbestos, followed by a 12-cm. section of anhydrous magnesium perchlorate.
9, 10, and 11. Manipulation of these taps enables air introduced into the combusion tube with the sample boat 12 to be removed with a reverse flush of nitrogen through tube 13.
14. Transparent quartz combusion tube, 2 mm. wall, 8 mm. i.d., with capillary inlet and outlet.
15. 14-cm. section carbon particles, 8–20 mesh.
16. 4-cm. section quartz chips, 8–20 mesh.
17. Electric furnace to maintain carbon particles at 1100° C. A continual check is kept on the temperature by means of a thermocouple in the annular space between furnace core and combusion tube.
18. Small trap for cooling in liquid oxygen.
19. Tail tap for outgassing trap at end of a series of runs.
20. Scavenging tube containing an 11 × 55 mm. section of 14–20 mesh indicating soda asbestos.
21. Oxidation tube containing a 9 × 110 mm. section of 16–30 mesh iodine pentoxide held between glass wool plugs and heated to 116° C by refluxing acetic acid in the mortar 22.
23. Absorption tube, 10 mm. i.d. with indented portion 10 cm. long, which is moistened with 20% sodium hydroxide for absorption of iodine.

Standard ground joints are used wherever possible; they are either sealed with a wax cement or greased and held by springs. Rubber connections are reduced to the minimum for flexibility in the apparatus; they are heavy walled and impregnated with paraffin wax.

When assembled the nitrogen flow is adjusted to 10 cc. per minute, the preheater and oxidation tube brought to operating temperature, the combustion tube bypassed, and a blank determination made on the oxidation tube. Properly conditioned iodine pentoxide shows no detectable blank during one hour.

The oxidation tube is now capped and the nitrogen passed through the combustion tube, discharging through the tail-tap. The furnace is switched on

and brought up to 1100° C. Heating overnight is usually sufficient to remove all volatile components from the carbon filling and to reduce the blank to its minimum value. During this period, the vaporization zone is also thoroughly heated with the movable burner.

The nitrogen stream is now passed through combustion and oxidation tubes, *i.e.*, as during an actual analysis, and a series of blank determinations made. This sweeping blank should be constant and preferably not greater than 0.05 cc. thiosulfate per 20 minutes. Higher blanks are usually due to nonvolatile impurities in the carbon filling. The remedy is to use a carbon containing not more than 0.01 per cent ash.

The blank correction applied to all results is determined by the same procedure as used in an actual analysis, except that no sample is placed in the boat. A small constant blank increment is usually observed when the vaporization zone is heated with the movable burner, but a preliminary changing of boats and reverse flush of nitrogen makes no detectable contribution to the blank.

IODINE PENTOXIDE

The determination of carbon monoxide by oxidation with iodine pentoxide has been reviewed by Ambler[12]. The preparation of a suitable grade of iodine pentoxide is best accomplished by heating pure iodic acid at 150° to 200° C, breaking up the product, and sieving out the required particle size. This is packed into the oxidation tube, which is then connected up in the assembly, and the final dehydration carried out *in situ* by heating to 230° to 240° C in a stream of pure nitrogen. The oxidation tube is ready for use when the iodine evolution falls to a minimum.

CARBON

Aluise, Hall, Staats, and Becker[8] have already indicated that two important requirements for a satisfactory carbon are an amorphous structure and a low ash content. There is no fundamental objection to the use of the more crystalline graphitic carbons; they are not satisfactory on practical grounds because of the much longer contact time required to convert carbon dioxide and water to carbon monoxide. The ash content is more significant because of its effect on the magnitude of the blank (Table I).

TABLE I

BLANK VALUES IN ML. *N*/100 THIOSULFATE PER 30 MINUTES AT 9 CC. NITROGEN PER MINUTE

Temperature (° C)	Ash content of carbon			
	Nil	0.03	0.17	0.62
960	—	—	0.06	0.11
1020	—	0.13	0.16	0.25
1050	—	—	0.24	0.38
1085	0.10	—	0.30	0.68

Most of the results presented have been obtained using a lampblack containing only 0.01 per cent ash and giving a blank value of 0.04 to 0.05 cc. of 0.1 *N* thiosulfate per 20 minutes. We have not yet succeeded in obtaining an absolute blank as claimed by Unterzaucher.

Results within ±0.2 of the theoretical oxygen content may be obtained, using higher ash carbons, but fictitious results are obtained when large samples

are vaporized in the determination of traces of oxygen. In this manner values as high as 0.4 per cent oxygen have been observed for a sample of purified naphthalene.

CONTROL ANALYSIS

When the apparatus delivers a sufficiently low blank the first test analysis is commenced by weighing into a platinum boat a sample containing 0.5 to 1 mg. of oxygen. The oxidation tube is capped, nitrogen passed in the reverse direction, and the sample introduced into the combustion tube. After five minutes the nitrogen is passed in the normal direction and the oxidation tube cap replaced by the absorption tube. The sample is now uniformly vaporized during 10 minutes and the movable burner extinguished when it reaches the furnace. After sweeping out for a further 10 minutes, the absorption tube is detached and the determination completed as described by Leipert[10].

Some typical results are quoted in Table II.

TABLE II

Compound	% Oxygen found				% Oxygen (theory)
Sucrose	51.2	51.6	51.4	51.4	51.4
β-Naphthol	11.25	11.2	11.1	11.15	11.1
p-Chloroacetanilide	9.5$_5$	9.5$_5$			9.4$_5$

The apparatus is next tested for its ability to yield consistently low results when comparatively large samples of hydrocarbons are vaporized (Table III).

TABLE III

Compound	Mg. sample	% oxygen
Naphthalene (B.D.H. analytical standard)	32	0.022
	63	0.022
	103	0.016
Paraffin oil (B.P.)	46	0.023

It is interesting to note that Unterzaucher found 0.026 and 0.024 per cent oxygen, respectively, for specially purified anthracene and paraffin oil. It has not yet been determined whether these oxygen contents are real, or represent the limit of accuracy of the method when applied to the determination of traces of oxygen.

The products of the reaction over carbon at 1100° C always contain traces of unsaturated hydrocarbons. Whether they are sufficient to interfere in a trace determination of oxygen probably depends on the type of carbon and purity of iodine pentoxide employed. If so, they are removed by cooling the trap (Figure 1 (18)) in liquid oxygen and, as a precautionary measure, the cold trap is retained when making oxygen determinations in the range 0 to 2 per cent.

On standing overnight, the main furnace is switched off and the nitrogen stream choked to 1 to 2 cc. per minute by means of a capillary on the oxidation tube. For longer periods the oxidation tube is capped, the preheater may be switched off, and the whole apparatus left under nitrogen. As a precautionary measure, in the event of an in-leak of moisture, the oxidation tube is always kept hot.

APPLICATION OF METHOD TO RUBBERS

It has been found best to take approximately 20 mg. of sample. Since each 0.03 cc. of 0.1 *N* thiosulfate then represents 0.01 per cent of oxygen, an accuracy

of ±0.02 may be obtained. Larger sample weights do not give a corresponding increase in precision and only result in a more rapid blockage of the reaction tube, due to carbon deposition.

NATURAL RUBBER

We first applied the method to pale crepe which had been subjected to increasing milling. Attempts had previously been made to detect any oxygen uptake by difference from careful microdeterminations of carbon, hydrogen, nitrogen, and ash. The superiority of the direct determination is apparent from Table IV.

TABLE IV

PALE CREPE. COMPARISON OF DIRECT AND INDIRECT OXYGEN DETERMINATION

Mooney value	% oxygen by difference. Tolerance ± 0.15		% oxygen direct						
			Series 1			Series 2			Mean
75	1.2	1.2	1.03	1.08	1.075	1.025		1.04	1.05
53	1.1	1.15		1.165			1.13		1.145
36	1.2			1.16			1.145		1.15
19	1.3	1.3		1.235		1.265		1.28	1.26

Series 1. No liquid oxygen trap.
Series 2. With liquid oxygen trap.

There is no significant difference in the result, whether or not unsaturates are removed before the carbon monoxide estimation. The corresponding oxygen contents found for napththalene were 0.02 and 0.03 per cent. The necessity, or otherwise, of the liquid oxygen trap depends on the results of test analyses with pure hydrocarbons, and also on the accuracy required in the determination.

We have been unable to duplicate these results either with pale crepe (Table V) or with smoked sheet (Table VI).

TABLE V

PALE CREPE. DIRECT DETERMINATION OF OXYGEN

				Mean % oxygen
Original	1.045	1.035		1.04
Dried in high vacuum	1.015	0.995		1.005
Acetone extracted	0.76	0.77	0.78	0.77
Milled: Mooney 75	1.165	1.15		1.155
Mooney 22	1.145	1.16		1.15

TABLE VI

SMOKED SHEET. DIRECT DETERMINATION OF OXYGEN

				Mean % oxygen
Original	1.355	1.43	1.42	1.40
Dried in high vacuum	1.42	1.43	1.37	1.41
Acetone extracted	1.13	1.20	1.17	1.17
Milled: Mooney 77	1.40	1.465	1.465	1.44
Mooney 47		1.43		1.43
Mooney 32		1.445		1.445
Mooney 22	1.43	1.465		1.445

No special precautions were observed to obtain representative samples. The probability of sampling errors and the question of oxygen uptake during mastication are subjects of further investigation.

The method is also applicable to rubber derivatives containing sulfur and halogen (Table VII).

TABLE VII

	% oxygen by difference	% oxygen direct		
Rubber hydrochloride	0.8 ± 0.3	0.80	0.79	0.81
Sulfur-vulcanized rubber	1.0 ± 0.3	1.15	1.17	

GUTTA-PERCHA

By providing samples of gutta-percha into which known proportions of oxygen had been introduced, J. L. Bolland has made it possible for us to check the accuracy of the method when applied to rubberlike materials (Table VIII).

TABLE VIII

OXIDATION OF GUTTA-PERCHA PURIFIED BY PRECIPITATION

Sample 1. 0.11 0.12 0.11 %O
Sample 2. 0.15 0.15 %O Mean 0.13 % O

Oxygen added (%)	Oxygen content (%)			
	Actual	Observed		
0.32	0.45	0.46	0.42	0.445
0.65	0.78	0.785	0.78	0.775
1.30	1.43		1.37	
1.66	1.79		1.70	

SUMMARY

The direct determination of oxygen in organic compounds by reduction with carbon on a microscale by the Unterzaucher method is described, together with criteria of purity for the carbon and iodine pentoxide reagents employed.

The method has been applied to rubbers and a relative precision of 2 per cent has been obtained *i.e.*: ±0.01 in the range 0 to 0.5% oxygen, ±0.02 in the range 0.5 to 1.0% oxygen, ±0.04 in the range 1.0 to 2.0% oxygen. For compounds containing larger percentages of oxygen, the method gives an absolute accuracy of ±0.2 or better.

The method is speedier and yields more accurate results than when oxygen is determined by difference or by hydrogenation. A single determination requires but 30 minutes.

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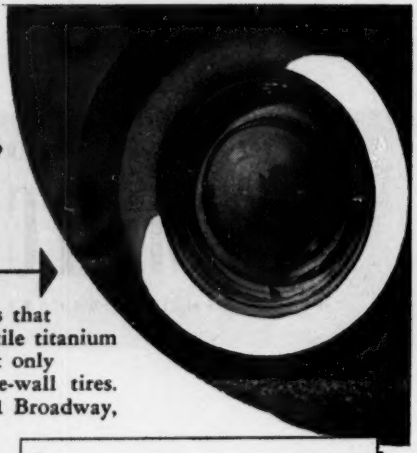

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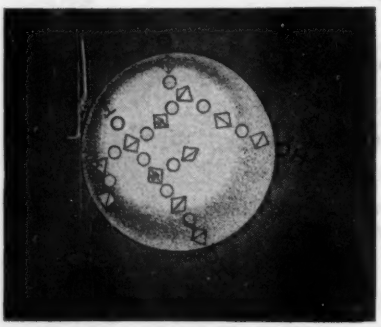

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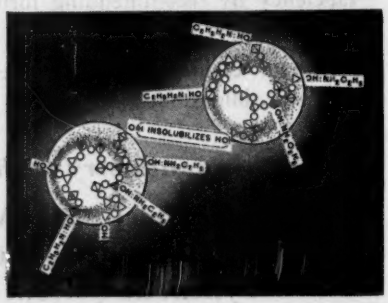

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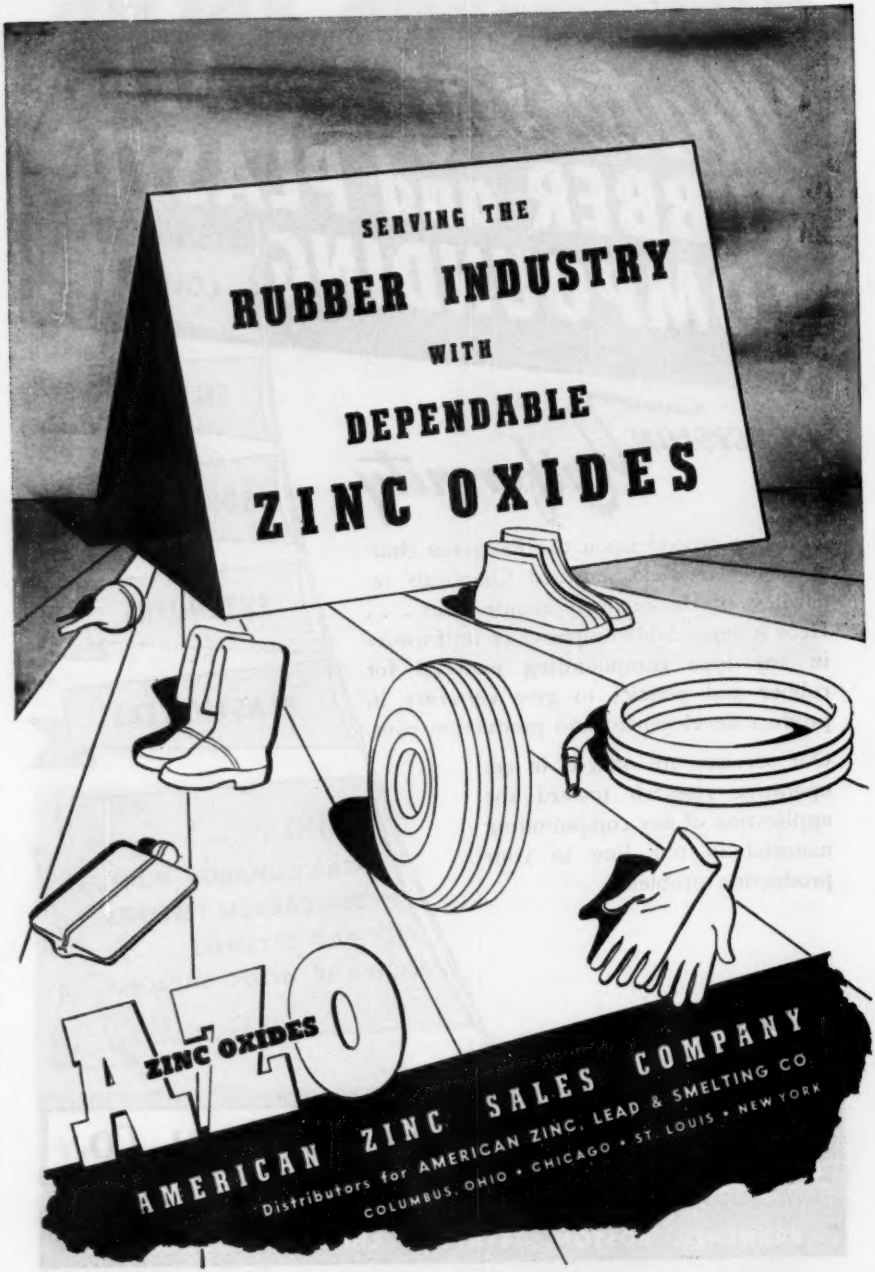
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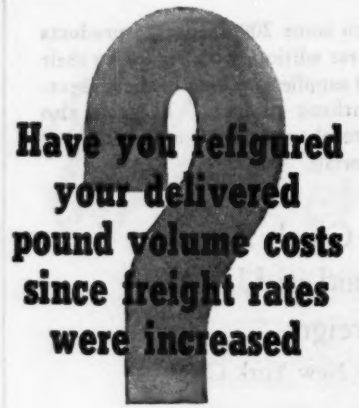

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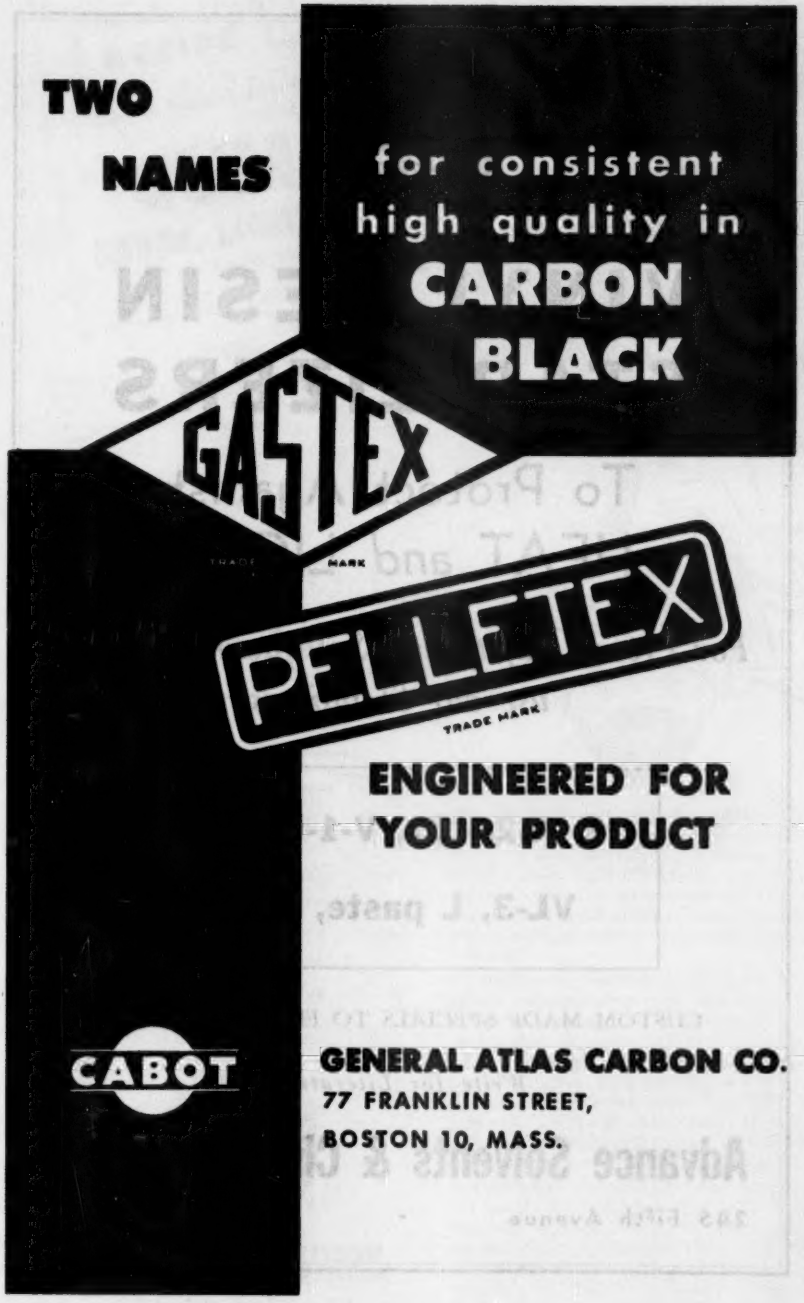
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RECIPE

Smoked Sheets	100.00
"CUMAR" Resin, Light EX Grade	10.00
"Philblack" A	62.50
Calcium Carbonate (Precipitated)	50.00
"Dixie" EF	25.00
Zinc Oxide	5.00
Stearic Acid	2.00
"Agerite" Alba	1.00
"Sunproof"	1.00
Sulfur	2.50
Benzothiazyl Disulfide	1.00
DOTG	0.25
Total	250.25

Specific Gravity	1.37
Rubber Hydrocarbon, % by Weight	38.5
Rubber Hydrocarbon, % by Volume	57.0
Mooney Viscosity, ML 4 min. @ 212. F.	57.0

Scorch Test—Press Cures @ 280 F.

Minutes	Cure
5	None
10	Slight
15	Fair

Press Cure at 316 F. (70 lb.)—15 Minutes:

Tensile and Hardness Data	Unaged	Aged 24 Hrs. @ 100 C.
Stress, 300%, psi.	1500	1600
Tensile, psi.	1900	1700
Elongation, %	480	310
Hardness, Shore A	79	82
Tear-Resistance, Angle, lb./1-in. thickness	185	145

Press Cure at 316 F. (70 lb.)—15 Minutes:

Abrasion Resistance, du Pont cc. lost/hp-hr.	275	300
Compression Set, 25% Constant Deflection, %	49	—
Resilience, Yerzley, 20% Deformation, %	44	33
Rebound, Goodyear-Healey, %	53.0	47.8
Contact Stain (24 hrs. @ 175 ± 2 F.)	Slight	—
Migration Stain (24 hrs. @ 125 ± 1 F.)	Slight	

Barrett

THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

*Reg. U. S. Pat. Off.

To confer efficient and safe processibility, and to impart smooth and rapid calendering and extruding properties, "CUMAR" resin, light EX grade, is an exceptionally effective processing aid. It has found wide application in the compounding of natural rubber and synthetic elastomers.

Its reinforcing feature modifies the nerve of the rubber, minimizes shrinkage, and prevents sagging and flattening in open steam and air cures. Its extending character improves physical properties, and permits higher filler loading, thereby reducing compounding costs. The light EX grade of "CUMAR" resin is also extremely valuable for improving cut-growth resistance, and hot and cold tear-resistance.

In the design of automotive and aeronautical parts, mechanical and proofed goods, flooring, matting, bumper and channel stocks, and in items which are to be used in contact with dark-colored enamels and lacquers, "CUMAR" resin, light EX grade, promotes quality along with economy.

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